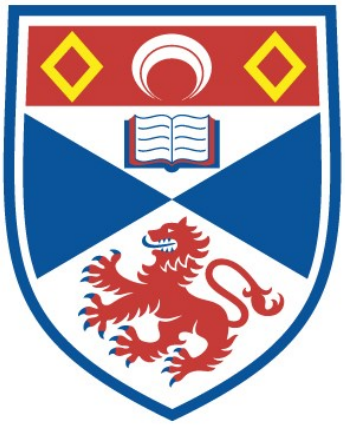
# N-NITROSOACYLARYLAMINES

Jemima Birrel Thomson

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



1968

# N-NITROSOACYLARYLAMINES

A Thesis

presented for the degree of

Doctor of Philosophy

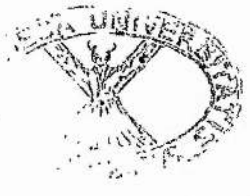
in the Faculty of Science of the

University of St. Andrews

by

Jemima Birrell Thomson, B.Sc.

United College of
St. Salvator and
St. Leonard, St. Andrews.



I declare that this thesis is my own composition, that the work of which it is a record has been carried out by myself, and that it has not been submitted in any previous application for a Higher Degree.

The thesis describes results of research carried out at the Chemistry Department, United College of St. Salvator and St. Leonard, University of St. Andrews, under the supervision of Professor J.I.G. Cadogan since the 1st October 1964, the date of my admission as a research student.

I hereby certify that Jemima Birrell Thomson, has spent twelve terms at research work under my supervision, has fulfilled the conditions of Ordinance No. 16 (St. Andrews) and is qualified to submit the accompanying thesis in application for the degree of Doctor of Philosophy.

Director of Research.

## ABSTRACT

The decompositions of N-nitrosoacylarylamines in benzene and in carbon tetrachloride have been investigated. The reaction products of N-nitrosobenzanilides parallel those of N-nitrosoacetanilides, carboxylic acids being the major products from almost all reactions carried out in both benzene and carbon tetrachloride. Carboxylic anhydrides, hitherto unreported products, have been isolated from reactions in carbon tetrachloride. The observed displacement of a bromo or nitro substituent in o- or p-positions in the amino moiety of the nitrosoamide by a chloride or benzoate ion during the formation of aryl halides and substituted phenyl benzoates is in contrast to Suschitzky's results, (Tetrahedron, 1962, 18, 1369).

In general, the major part of the reaction appears to be abstraction by a carboxylate anion of hydrogen from the o-position in the amino moiety of the nitrosoamide to form the carboxylic acid. However, when both o-positions in the amino moiety of the nitrosoamide are substituted, the reaction proceeds primarily by nucleophilic displacement of a substituent by the carboxylate anion.

The decomposition of N-nitrosoacetanilide in carbon tetrachloride gives a benzynoid-type adduct with 2,3,4,5-tetraphenylcyclopentadienone, with consequent suppression of the formation of chlorobenzene, which is a major product

from a reaction carried out in the absence of the above diene. Appropriate benzynoid-type adducts are also formed in reactions of N-nitrosobenzanilides with 2,3,4,5-tetraphenylcyclopentadienone and with anthracene, but not with furan. By the use of substituted N-nitrosobenzanilides, it has been shown that, for appreciable adduct formation with 2,3,4,5-tetraphenylcyclopentadienone, a substituent must be in the m-position in the amino moiety, i.e. o- or p- to the hydrogen which is being removed in the formation of the carboxylic acid. The nature of the acyl moiety of the molecule has some influence on the formation of the adduct, but the nature of the solvent appears to have little influence on the yield of adduct formed. In reactions in which high yields of benzynoid-type adducts are obtained, the only other major product isolated is the appropriate carboxylic acid. True aryne intermediates are discounted, and it is suggested that the intermediate is dipolar in nature.

A reaction scheme involving radicals, previously suggested by Rüchardt et al. (Tetrahedron Letters, 1964, 3623), can be modified to account for the reaction in benzene. The reaction in carbon tetrachloride, however, appears to follow a different reaction path, and probably involves radicals to a slight extent only, the main reaction being ionic.

ACKNOWLEDGEMENTS

I should like to thank Professor J.I.G. Cadogan for suggesting the topic of research and for his continued advice and encouragement during the period in which the work was carried out.

In addition, I am indebted to Dr. D.M. Smith for his invaluable advice.

I should like to thank also Dr. C. Thomson for the production of E.S.R. spectra, Professor C.W. Rees for samples of 5-methyl and 6-methyl-1,2,3,4-tetraphenylnaphthalene, and Drs. R.K. Mackie and J.T. Sharp for helpful discussions.

Thanks are due also to the Science Research Council for the award of a Research Studentship for the period during which this work was carried out.

CONTENTS

Page No.

INTRODUCTION

This thesis describes reactions of N-nitrosoacylarylamines in benzene and carbon tetrachloride carried out with a view to the detection of aryl radicals and/or arynes or arynoid intermediates. Accordingly, the introductory section of the thesis includes a summary of the known reactions of aryl radicals, arynes and N-nitrosoacylarylamines.

## 1. SOURCES OF ARYL RADICALS.

The usual methods for the production of aryl radicals involve either thermolysis or photolysis of appropriate compounds.

### A. THERMOLYSIS.

i) Diazohydroxides and diazoacetates (The Gomberg Reaction):[1,2,43]

e.g. $Ar{\cdot}N_2^+\ Cl^- + NaOH \longrightarrow Ar{\cdot}N_2{\cdot}OH \xrightarrow{Ar^1H} Ar{\cdot}Ar^1 + N_2 + H_2O$

ii) Arylazotriphenylmethanes:[9,10,11]

e.g. $Ph{\cdot}N{:}N{\cdot}CPh_3 \longrightarrow Ph{\cdot} + N_2 + {\cdot}CPh_3$.

iii) Diazonium salts, such as the chloride[3,4] and trifluoroacetate[5] give radicals, probably by homolysis of the covalent form which is thought to be in equilibrium with the ionic form.

e.g. $Ph{\cdot}N_2^+Cl^- \rightleftharpoons Ph{\cdot}N{:}N{\cdot}Cl \longrightarrow Ph{\cdot} + N_2 + {\cdot}Cl$.

iv) Diazoanhydrides:[6]

e.g. $Ar{\cdot}N_2{\cdot}O{\cdot}N_2{\cdot}Ar \longrightarrow Ar{\cdot} + N_2 + {\cdot}O{\cdot}N_2{\cdot}Ar$

v) 1-Aryl-3,3-dialkyltriazens:[7]

e.g. $Ar{\cdot}N{:}N{\cdot}N{\cdot}R_2 \longrightarrow Ar{\cdot} + N_2 + {\cdot}NR_2$

vi) Aromatic amines and amyl nitrite:[8] the reaction probably involves the formation and homolysis of a diazo compound.

e.g. $PhNH_2 + Am{\cdot}ONO \longrightarrow Ph{\cdot}N{:}N{\cdot}OAm \longrightarrow Ph{\cdot} + N_2 + {\cdot}OAm$.

vii) Peroxides:[9,11-15]

e.g. $Ar\cdot CO\cdot O\cdot O\cdot CO\cdot Ar \longrightarrow Ar\cdot COO\cdot \longrightarrow Ar\cdot + CO_2$.

viii) Lead tetrabenzoate,[16] phenyl iodosobenzoate[16,18] and silver halide dibenzoates.[17]

e.g. $Pb(O\cdot CO\cdot Ph)_4 \longrightarrow Pb(O\cdot CO\cdot Ph)_2 + 2Ph\cdot CO_2\cdot$

$PhI(O\cdot CO\cdot Ph)_2 \longrightarrow PhI + 2Ph\cdot CO_2\cdot$

$2Ph\cdot CO\cdot O\cdot Ag + I_2 \longrightarrow (Ph\cdot CO\cdot O)_2AgI \longrightarrow 2Ph\cdot CO_2\cdot$

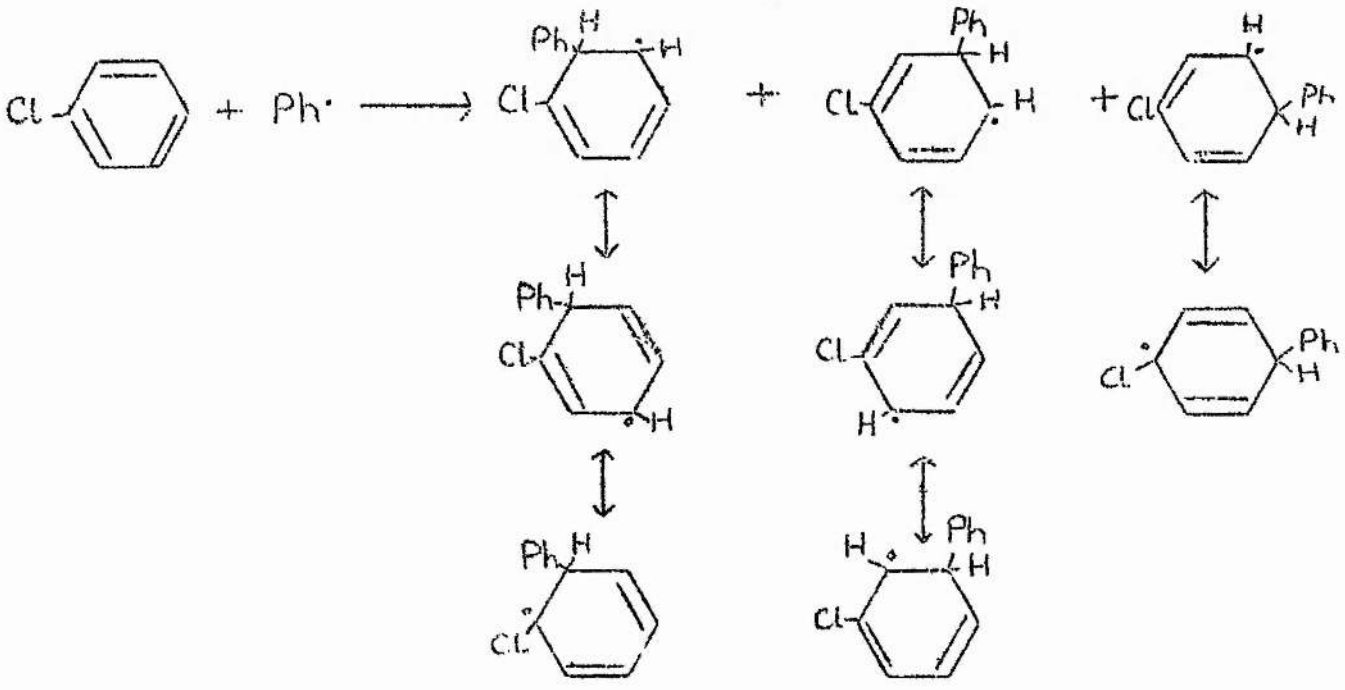
ix) N-Nitrosoacylarylamines: These compounds are the subject of this thesis and they will be discussed later. (p. 6 ).

B. PHOTOLYSIS.

Irradiation of diphenylmercury[19] or triphenylbismuth[20] with ultraviolet light gives rise to phenyl radicals. Certain iodo compounds[21] also decompose on irradiation.

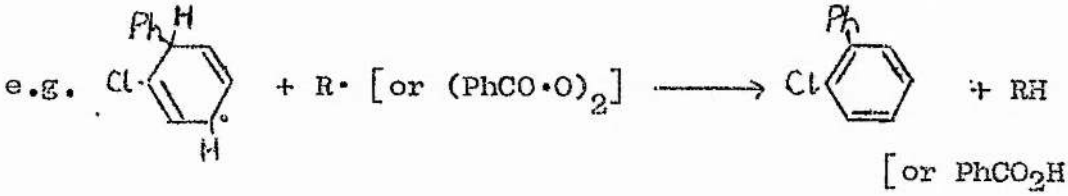
## 2. REACTIONS OF ARYL RADICALS

a) With Aromatic Substrates. The overall reaction of an aryl radical with an aromatic substrate is generally one of substitution. The first step in the reaction is addition of the radical (Ph·) to the substrate (e.g. PhCl) to form a sigma-complex.[15,22] Addition takes place in the o, m, and p-positions[12,13,14] in accord with the insensitivity of homolytic reactions for electronic influences.



The radicals so produced in the initial addition process can then undergo one or more of the following reactions:

i) Abstraction of a hydrogen atom by any radical R· present in the system, or by reaction with an oxidising agent, to give a biaryl.

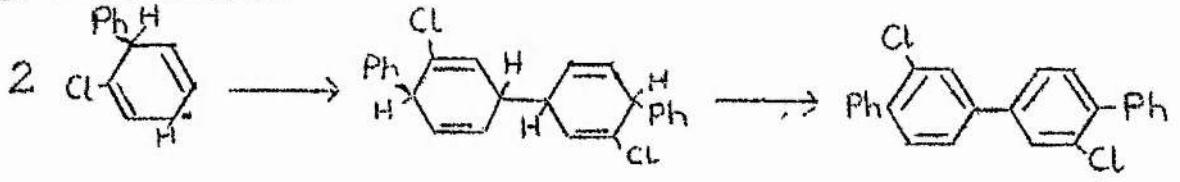


ii) Disproportionation to give a biaryl and a dihydrobiaryl.[15,24]

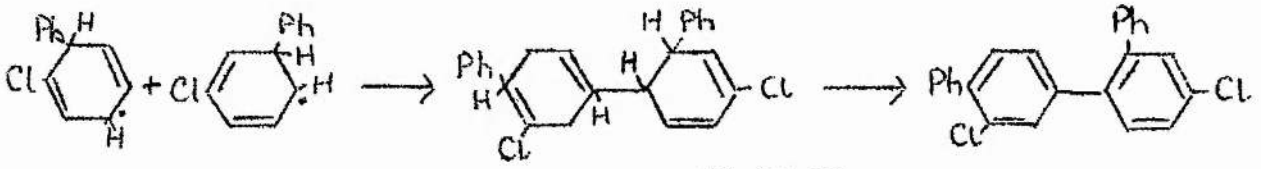
e.g. 

iii) Dimerisation or coupling to give a tetrahydroquaterphenyl,[13,15,23] which can be oxidised to a quaterphenyl.

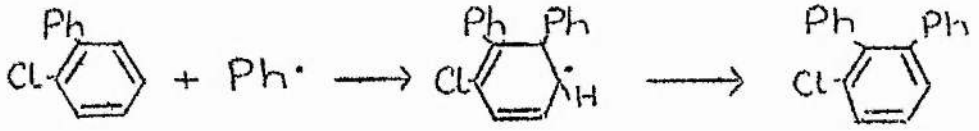
e.g. Dimerisation:



Coupling:



iv) Formation of a terphenyl derivative[13,15,23] by attack of an aryl radical on a biaryl,

e.g. 

together with products from attack at the other positions.

When diaroyl peroxides are used as arylating agents, each of the above types of reaction occurs, major products (30-60%) being an isomeric mixture of biaryls, in which the o-isomer usually predominates. However, when using N-nitrosoacylarylamines as the radical source, no dihydrobiaryls or quaterphenyls are isolated. Reaction schemes to account for the absence of these compounds have been proposed recently by Rüchardt et al.[2,25] and by Perkins et al.[77,78] [See section on nitrosoacylarylamines (pp.20-22 )].

b) With Aliphatic Compounds.

The reaction which takes place between an aryl radical and an aliphatic substrate is one of abstraction.[26]

e.g. $Ar\cdot + RH \longrightarrow ArH + R\cdot$

$Ar\cdot + CHCl_3 \longrightarrow ArH + \cdot CCl_3$

$Ar\cdot + CCl_4 \longrightarrow ArCl + \cdot CCl_3$

In polyhalogenomethanes, however, there are obvious differences between the reactions of peroxides and arylazotriphenylmethanes on the one hand and N-nitrosoacetanilides and diazonium compounds on the other. Thus, decomposition of benzoyl peroxide in carbon tetrachloride gives a high yield of chlorobenzene, and the trichloromethyl radicals appear both as the dimer, hexachloroethane, and also as p-trichloromethylbenzoic acid.[27,34,19(b)] However, in the decomposition of N-nitrosoacetanilide in carbon tetrachloride, benzenediazonium chloride is formed as an intermediate, and the products of this reaction include a high yield of acetic acid, a fair yield of chlorobenzene and a trace of phenol, but no trace of the trichloromethyl radical is found.[1,28,29,30] No hexachloroethane is isolated in reactions of phenylazotriphenylmethane[125] or in reactions of amyl nitrite with aromatic amines[157] in carbon tetrachloride.

In chloroform, decomposition of peroxides leads to hydrogen abstraction only, while decomposition of nitrosoacetanilide gives rise to both hydrogen and chlorine abstraction.[30,32,33]

i.e. $(Ph\cdot CO\cdot O)_2 + CHCl_3 \longrightarrow PhH + \cdot CCl_3$

$Ph\cdot N\cdot (NO)\cdot CO\cdot CH_3 + CHCl_3 \longrightarrow PhH + PhCl$

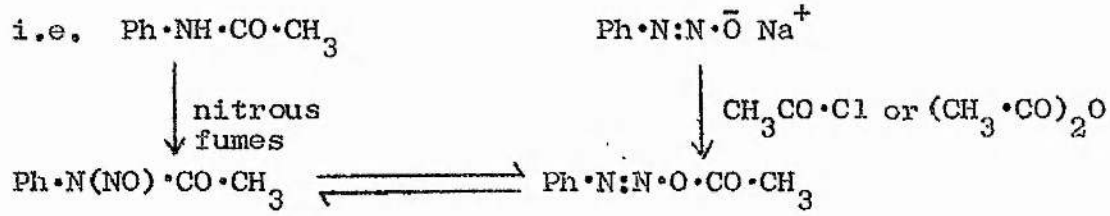
All radical sources give rise to abstraction of both hydrogen and halogen from bromoform.[34] Radicals from nitrosoacetanilide abstract both bromine

and chlorine from bromotrichloromethane,[34] but other radical sources show almost negligible chlorine abstraction from this substrate.

The reactions of N-nitrosoacylarylamines therefore differ in many respects from those of aroyl peroxides. In the latter case, the reactions are well understood, and can be rationalised in terms of the known reaction of aryl radicals. In the former case, less is known about the reactions. This lack of knowledge prompted this investigation.

## 3. N-NITROSOACYLARYLAMINES

N-Nitrosoacetanilide was first prepared by Fischer[35] in 1876 by the action of nitrous fumes on acetanilide. An identical compound was later prepared[36] by the reaction of an acylating agent with an alkaline diazonium solution. It was therefore suggested by various workers[36-41] that N-nitrosoacylarylamines were tautomeric with the diazoesters.




The use of N-nitrosoacylarylamines as arylating agents was demonstrated by Kuhling[38] in 1895 by the formation of 4-nitrobiphenyl in the reaction of N-nitroso-4-nitroacetanilide in benzene. A study of the reaction of N-nitrosoacetanilide in benzene by Bamberger[40] showed the products to be biphenyl (50%), acetic acid and nitrogen. A different type of product, an ester, was later isolated in a similar reaction.[42]

$$Ph\cdot CO\cdot N(NO)\cdot CH_2\cdot Ph \xrightarrow{PhH} Ph\cdot CO\cdot O\cdot CH_2\cdot Ph + N_2.$$

Renewed interest in N-nitrosoacylarylamines was aroused in 1934 as a result of the extensive kinetic investigations of Hey et al.[1,28,29] These workers found that, in reactions of N-nitrosoacylarylamines in aromatic solvents, the usual laws of electrophilic substitution were not applicable.[6,37,39,40] Substitution took place at the ortho and para positions, irrespective of the orientating influence of a substituent already present, and, in that respect, these reactions were similar to the Gomberg reaction[43] and to reactions of peroxides.[9,41] Grieve and Hey[1,28] therefore postulated a neutral radical, Ph·, as an intermediate in order to rationalise these results.

The rate of decomposition of N-nitrosoacylarylamines, as measured by the rate of nitrogen evolution, was found to conform to a unimolecular, first order law, and to be independent of substrate. The rate-determining step must therefore have been the production of the radical Ph·, and not subsequent reaction of Ph·. Grieve and Hey suggested the rate-determining step to be homolysis of the diazoester, i.e.

$$Ph{\cdot}N(NO){\cdot}CO{\cdot}CH_3 \xrightarrow{\text{fast}} Ph{\cdot}N{:}N{\cdot}O{\cdot}CO{\cdot}CH_3 \xrightarrow{\text{slow}} Ph^{\circ} + N_2 + CH_3COO^{\cdot}$$

Support for the radical nature of the reaction came from further work by Waters and Hey.[32,44] Decomposition of N-nitrosoacetanilide in dry aromatic solvents was frequently found to yield benzene, obviously by a non-ionic route, while decomposition in solvents such as carbon tetrachloride and carbon disulphide, in the presence of metals, resulted in water-soluble solids, chiefly acetates.[32] The occurrence of acetic acid, and, in some cases, carbon dioxide, was taken as proof of the presence of the acetoxy radical, rather than the acetate ion which would

not be expected to decarboxylate. Initiation by N-nitrosoacetanilide of addition polymerisation,[45] known to be radical induced, and incorporation of the aryl moiety of the molecule into the polymer, indicated the intermediacy of active free aryl radicals.

The radical hypothesis was challenged by Hodgson[46] who preferred ionic mechanisms, but Hey and Waters[47] pointed out that, while ionic mechanism might be operative, radical mechanisms were essential to explain their results. They were supported by various workers[14,48,49,50] who found that the nature of substituents in the aromatic substrate had little influence on the orientation of substitution by the aryl moiety of the nitrosoamide.

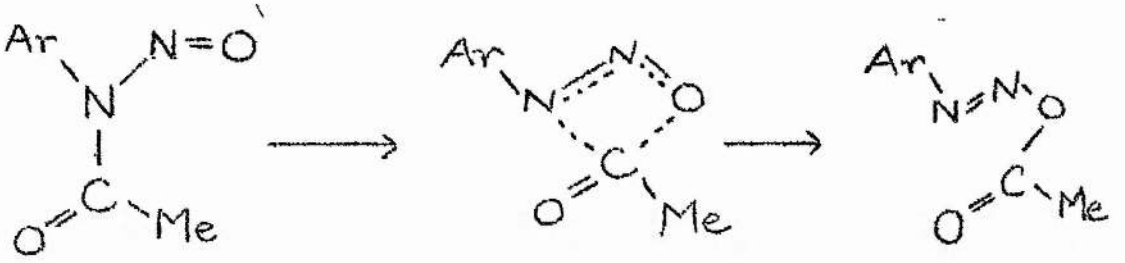
Hey's mechanism, i.e. homolysis of the diazoester as the rate-determining step, was accepted until 1949, when Huisgen and Horeld[51,52] measured the rate of coupling with β-naphthol in the reaction of N-nitrosoacetanilide with benzene, and found it to be identical to the rate of nitrogen evolution. The only apparent explanation for this equality of rates was that the rate-determining step occurred prior to the production of the diazonium cation.

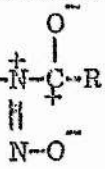
$$\text{i.e. } Ph\cdot N(NO)\cdot CO\cdot CH_3 \xrightarrow{\text{slow}} Ph\cdot N{:}N\cdot O\cdot COCH_3 \begin{cases} \xrightarrow{\text{fast}} Ph\cdot + N_2 + \cdot O\cdot CO\cdot CH_3 \\ \xrightarrow{\text{fast}} PhN_2^+ + {}^-O\cdot CO\cdot CH_3 \end{cases}$$

Soon afterwards, De Tar[53] reached the same conclusions.

Huisgen[54] suggested that the acyl migration from nitrogen to oxygen proceeded via an intramolecular rearrangement, leading to the trans

diazoester:

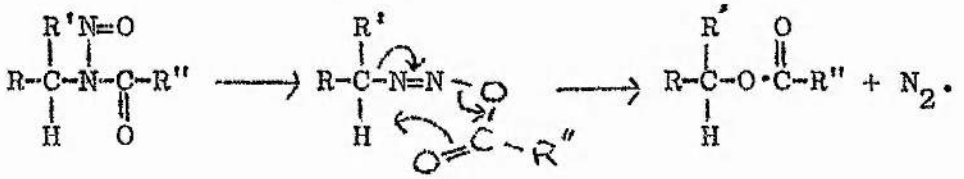
i.e. 

He discounted free ions in the intermediate state on the grounds that the reaction was carried out in non-polar solvents, and also because the rate was independent of substituents in m or p-positions in the amino moiety. o-Substituents hindered the reaction, presumably by preventing the benzene ring and the four-membered ring in the intermediate state being co-planar.[54] After further kinetic work, Hey et al.[55] agreed with Huisgen, but Heyns and Babenburg[56], on the other hand, maintained that substituents would show some influence on the reaction rate. They postulated a partial dipolar structure in the intermediate state,  , which they supported by ultraviolet spectral evidence.

Further evidence for the existence of a trans-isomer was the formation of indazoles from reactions of o-methyl-N-nitrosoacetanilide[57]. The diazoester must be in the trans-configuration for this reaction to occur.

The diazoester was found to decompose by a variety of routes, depending on the reaction conditions. N-Nitrosoacylarylamines in organic solvents gave biaryls as the major product of the reaction, but

N-nitrosoacylalkylamines gave esters and/or olefins.[59,60] Huisgen attributed the ester formation to purely ionic mechanisms[59] and later to a cage effect.[51] White[60] viewed it rather as a rolling of electrons. Finding that optically active materials often retained their configuration, he proposed, as part of the reaction, the following scheme:

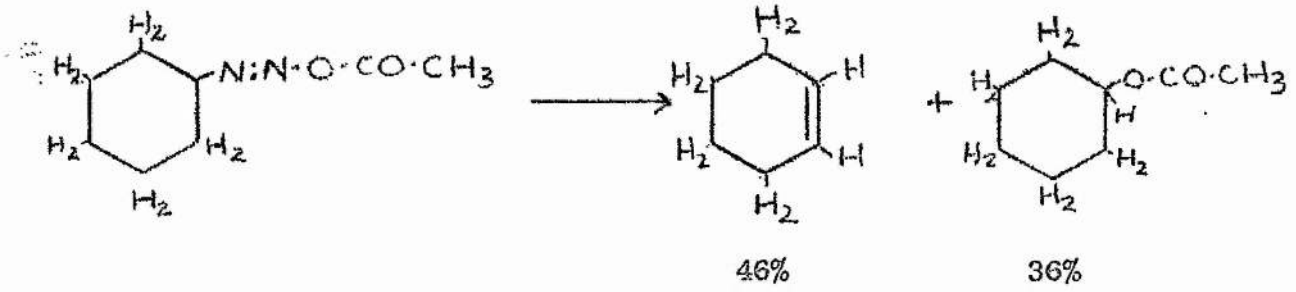


Radical intermediates were rejected on the basis that carbon dioxide would have been produced if the acetoxy radical had been present.[63] In a polar solvent, free ions could be present, and both intramolecular (as above) and intermolecular (ionic) rearrangements might operate together.[61] In non-polar solvents, however, ions would be unfavourable, but cross-over products were found in reactions using isotopically labelled oxygen.[61] i.e.

$$R\cdot N(NO)\cdot CO\cdot R' + R''\cdot N(NO)\cdot C\overset{\bullet}{O}\cdot{}^{18}R' \longrightarrow R\cdot CO\cdot{}^{18}\overset{\bullet}{O}\cdot R' + R''\cdot CO\cdot{}^{18}\overset{\bullet}{O}\cdot R'$$

White[61] therefore, further postulated that the diazoester might cleave to yield a diazoalkane and a carboxylic acid, which could then combine to form the ester, and could form cross-over products.

In reactions of nitrosoacylalkylamines the major products were olefins.[61] Huisgen's results[62] from experiments using nitrosoacylalkylamines containing secondary alkyl groups, especially the cyclohexyl group, are of special interest. These are exemplified overleaf:




This result appears to be analogous to our observations, described later, where reaction took place by loss of nitrogen and abstraction of hydrogen. The presence of olefins in the reaction mixture suggested to Huisgen a partial polar mechanism for nitrogen evolution, even in non-polar solvents. Polar and radical reactions must therefore have taken place simultaneously.

Homolysis of the diazoester would give rise to an acetoxy radical. In all reactions there was a marked absence of carbon dioxide,[49,51,60] the usual reaction for the acetoxy radical being immediate decomposition to a methyl radical and carbon dioxide.[63] The acetoxy moiety of the molecule appeared, rather, as acetic acid. Further, the aryl radicals produced from N-nitrosoacetanilide did not give dihydrobiaryls as did those from peroxides,[66] nor did they show any appreciable isotope effect in the phenylation of benzene and deuterobenzene.[67] De Tar[49] attributed this unusual behaviour to the high reactivity of the radicals from nitrosoacetanilide, while Huisgen postulated that actual free radicals were not involved, but that the acetoxy radical obtained a hydrogen atom

within a complex of reactant and solvent molecules.[51,64] Hey et al.[30,39] and Eliel et al.[66,67,68] suggested a "cage effect" in these reactions, believing that, while radicals from peroxides were sufficiently stable to diffuse away before reacting further, those from nitrosoacetanilide were constrained by a solvent cage and so reacted with the solvent before they had a chance to decarboxylate. The cage effect was further supported by the work of Overberger and Marullo.[65]

Eliel,[69] however, later withdrew his cage theory after the decomposition of nitrosoacetanilide in benzene in the presence of a low concentration of iodine was shown to give iodobenzene (85%). The phenyl radicals had been scavenged by the iodine, and this could not have occurred had the radicals been in a solvent cage. Further opposition to the cage effect came from Denny and Applebaum.[70] Recently, Rüchardt[25] suggested that the acetate ion, and not the radical, was involved in the reaction (see p. 15). No carbon dioxide would be expected in such circumstances.

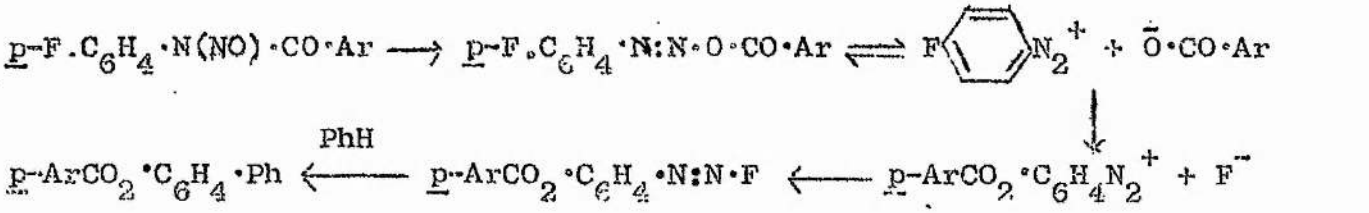
In view of the general acceptance of ionic as well as radical mechanisms, the original scheme proposed by Huisgen was modified[53,71]:

$$Ph\cdot N\cdot(NO)\cdot CO\cdot R \xrightarrow{slow} Ph\cdot N{:}N\cdot O\cdot CO\cdot R$$

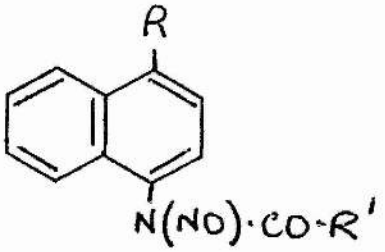
$$Ph\cdot N{:}N\cdot O\cdot CO\cdot R \xrightarrow{fast} Ph\cdot + N_2 + R\cdot COO\cdot$$

$$Ph\cdot N{:}N\cdot O\cdot CO\cdot R \xrightarrow{fast} Ph\cdot N_2^{+} + R\cdot CO_2^{-} \longrightarrow Ph^{+} + N_2 + R\cdot CO_2^{-}$$

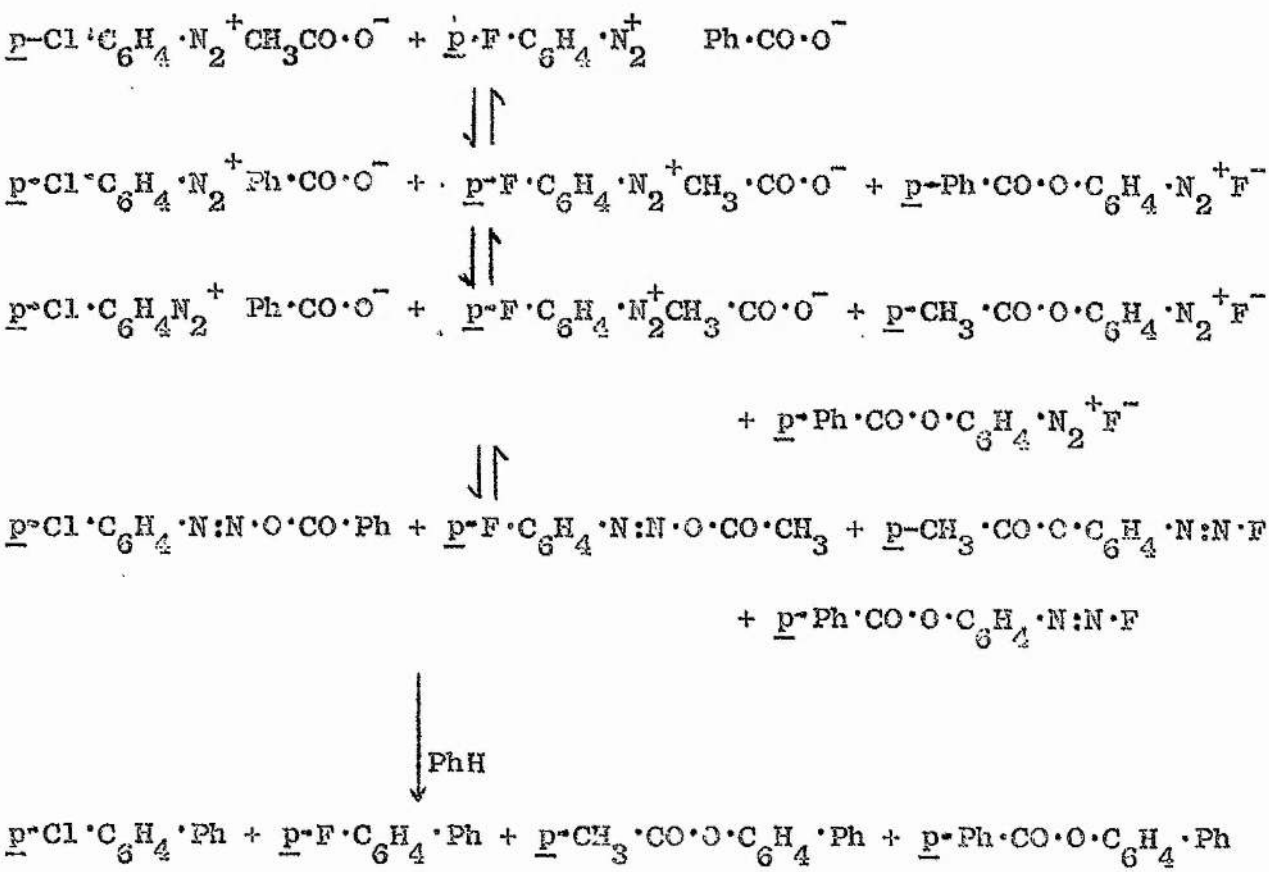
The heterolytic path was further investigated by Barben and Suschitzky,[72] who found that the reaction of N-nitroso-p-fluoroacetanilide in benzene yielded 4-acetoxybiphenyl as well as the expected 4-fluorobiphenyl. Similar results were obtained using N-nitrosobenzanilides. The mechanism proposed involved ionic intermediates in part[72,73]



There was no displacement of fluorine in the meta position, and no displacement of any other halogen. The unique behaviour of the fluoro compound was attributed to the marked electronegativity of the fluorine. These workers saw no reason for ion pairs to be absent in other N-nitrosoacylarylamines, however, and demonstrated their existence by allowing mixtures of N-nitroso-p-chloroacetanilide and N-nitroso-p-fluorobenzanilide to decompose in benzene, with the subsequent isolation of the cross-product, 4-acetoxybiphenyl, as shown:




(I)




In reactions of correspondingly substituted N-acetyl-N-nitroso-naphthylamines (I), chlorine, bromine and fluorine were all replaced by the acetate ion.

Suschitzky et al.[74] postulated a diazoanhydride as a possible intermediate to explain the production of acyl fluoride from such reactions.

e.g. p-R·CO·O·C6H4·N2+ F− + p-F·C6H4·N:N·O·CO·R ⟶ R·CO·F
+ p-F·C6H4·N2·O·N2·C6H4·O·COR(p)

Diazoanhydrides had been suggested as early as 1896 by Bamberger[6] to

be intermediates in the decomposition of N-nitrosoacylarylamines.

The diazoanhydride was the main intermediate in the reaction sequence for the decomposition of N-nitrosoacylarylamines in benzene proposed by Rüchardt[25] to explain the absence of the acetoxy radical. The absence of dihydrobiphenyls and quaterphenyls was explained by the presence of a diazotate radical, produced by homolysis of the diazoanhydride, which was assumed to scavenge the cyclohexadienyl radicals, preventing their disproportionation and dimerisation. The reaction sequence was as shown:

$$Ph\cdot N(NO)\cdot Ac \longrightarrow Ph\cdot N{:}N\cdot OAc \rightleftharpoons Ph\cdot N_2^{+} + \bar{O}Ac$$

$$Ph\cdot N{:}N\cdot OAc + \bar{O}Ac \longrightarrow Ph\cdot N_2O^{-} + Ac_2O$$

$$Ph\cdot N_2^{+} + Ph\cdot N_2\bar{O} \longrightarrow Ph\cdot N_2\cdot O\cdot N_2\cdot Ph \longrightarrow N_2 + Ph\cdot + Ph\cdot N_2O\cdot$$

$$Ph\cdot + PhH \longrightarrow \text{  } \xrightarrow{Ph\cdot N_2\cdot O\cdot} Ph\cdot Ph + Ph\cdot N_2\cdot OH$$

$$Ph\cdot N_2\cdot OH + AcO^{-} \longrightarrow Ph\cdot N_2\cdot O^{-} + AcOH.$$

The acetate ion and not the acetoxy radical participates in the reaction. Rüchardt supported this mechanism by E.S.R. studies.[75] The spectrum observed was said to agree with that computed for the phenyl diazotate radical, $Ph\cdot N{:}N\cdot O\cdot$. E.S.R. spectra were also obtained for p-$Cl\cdot C_6H_4\cdot N{:}N\cdot O\cdot$, p-$F\cdot C_6H_4\cdot N{:}N\cdot O\cdot$, p-$Me\cdot C_6H_4\cdot N{:}N\cdot O\cdot$, p-$Bu^t\cdot C_6H_4\cdot N{:}N\cdot O\cdot$, p-$D\cdot C_6H_4\cdot N{:}N\cdot O\cdot$ and $Ph\cdot N^{15}{:}N\cdot O\cdot$ from the appropriate N-nitrosoacetanilides.[76] The E.S.R. spectrum of the isotopically labelled nitrosoacetanilide indicated that there was no interchange of the nitrogen,

i.e. $Ph\cdot N^{15}(NO)\cdot CO\cdot Me \longrightarrow Ph\cdot N^{15}{:}N\cdot O\cdot$ entirely.

Recently, Perkins et al.[77] attributed this E.S.R. spectrum to the structure (A) $Ph-\underset{|}{N}-O\cdot$ suggesting that splittings from phenyl
(B) $Ph-\underset{|}{N}-CO-CH_3$,

group (B) were negligible. This structure was supported when the same spectrum was obtained[78] from a mixture of nitrosobenzene and N-bromoacetanilide in benzene. The radical shown above would be common to both reactions. Spectra from other substituted nitroso compounds supported this type of intermediate, which could act as an oxidant as shown:

$$PhN{:}N\cdot OAc \longrightarrow Ph\cdot + N_2 + \cdot OAc$$

$$Ph\cdot + PhN{:}N\cdot OAc \longrightarrow Ph-\underset{|}{N}-O\cdot \quad (Ph-N-COCH_3)$$

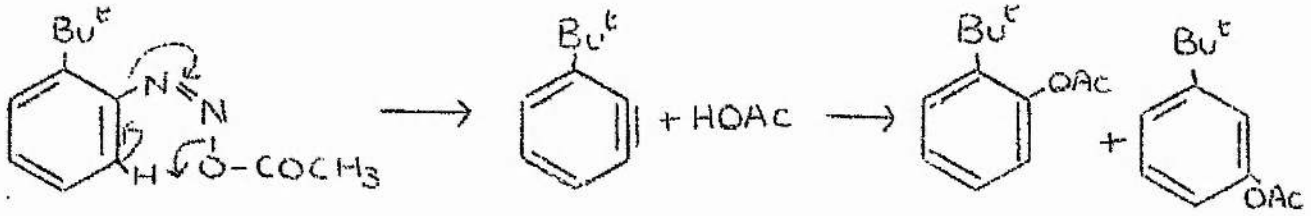
$$Ph\cdot Ph + Ph-\underset{|}{N}-OH \quad (Ph-N-COCH_3)$$

$$PhN{:}N\cdot OAc + Ph-\underset{|}{N}-OH \longrightarrow Ph-\underset{|}{N}-O\cdot + Ph\cdot + N_2 + AcOH$$
$$(Ph-N-COCH_3) \qquad (Ph-N-COCH_3)$$

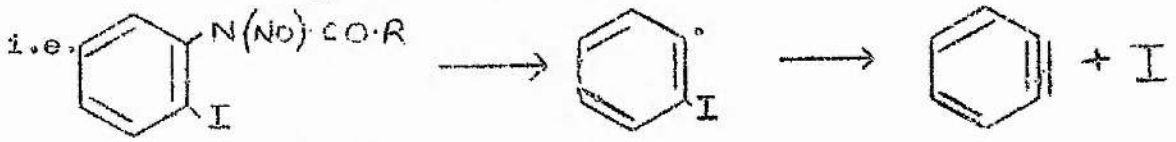
An identical E.S.R. spectrum was obtained from the reaction of p-chloro-N-nitrosoacetanilide and nitrosobenzene, showing that the splittings of ring (B) must be negligible.

It is clear, therefore, that uncertainty still surrounds the reactions of N-nitrosoacylarylamines in aromatic solvents. Further, anomalies which are not explicable by either of the above mechanisms also exist. Thus, in the decomposition of o-t-butyl-N-nitrosoacetanilide in benzene,

o- and m- t-butylphenyl acetates, and not 2-t-butylbiphenyl, were the main products.[48,79] The presence of an aryne intermediate was postulated[80] to account for the mixture of esters. It was suggested that the t-butyl group, being large, would constrain the molecule so that the cis-isomer of the diazoester would be formed. This would then undergo decomposition, by either a concerted or a homolytic process, to give 3-t-butylbenzyne and acetic acid, which, being in close proximity, would react to yield a mixture of esters.




Smaller groups in the ortho position would not constrain the molecule sufficiently to produce the cis-isomer, and hence no aryne would result. In the presence of anthracene, a known aryne trap,[81] 2-t-butyltriptycene was isolated, which seemed to support the proposed mechanism. This reaction is at present under extensive investigation.[82] Recently it has been reported[83] that o-iodo-N-nitrosoacylarylamines gave rise to an aryne intermediate by a free radical pathway, involving loss of an iodine atom from an o-iodophenyl radical.




The isolation of 1,2,3,4-tetraphenylnaphthalene from reactions carried out in the presence of 2,3,4,5-tetraphenylcyclopentadienone was taken to be proof of the intermediacy of an aryne.

The anomalous reactions of N-nitrosoacylarylamines which have yet to be explained are:

1. In carbon tetrachloride, benzenediazonium chloride is formed as an intermediate,[1,28,29,30] and acetic acid is the main product, with a smaller amount of chlorobenzene. Although hexachloroethane (the dimer of the trichloromethyl radicals) is identified in reactions using peroxides as the radical source, no trace of the trichloromethyl radical is found in reactions of N-nitrosoacetanilide[27,31] in carbon tetrachloride. Much tar is formed.

2. In benzene, no dihydrobiphenyls or quaterphenyls are isolated.

3. No carbon dioxide is evolved on decomposition in any solvent.

4. Radicals produced from nitrosoacetanilide abstract both chlorine and hydrogen from chloroform, while those from peroxides abstract only hydrogen.[30,32,33] Radicals from all sources abstract both bromine and hydrogen from bromoform.

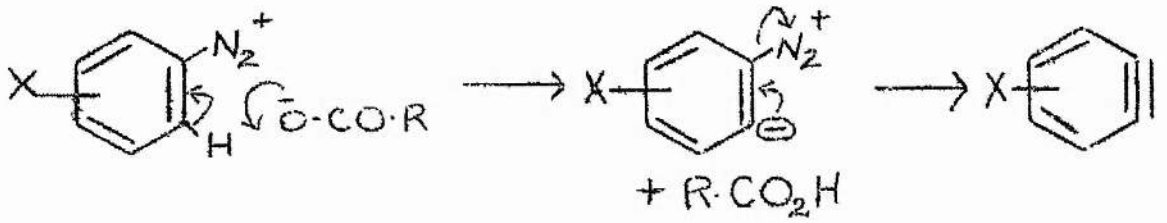
5. When nitrosoacetanilide is used as the radical source, both bromine and chlorine are abstracted from bromotrichloromethane, but other radical sources show almost negligible chlorine abstraction.

6. o-t-Butyl- and o-iodo-N-nitrosoacetanilides appear to react via an intermediate aryne.

7. In the phenylation of pyridine, radicals from nitrosoacetanilides give different isomer ratios from those from the other radical sources.[16(b)]

The outstanding anomalies mentioned above involve the formation of acetic acid and, in two cases, the possible formation of an aryne.

It was of interest therefore to investigate the possibility that aryne or arynoid intermediates might be formed in decompositions of N-nitroso-acylarylamines in general, possibly via the following route:



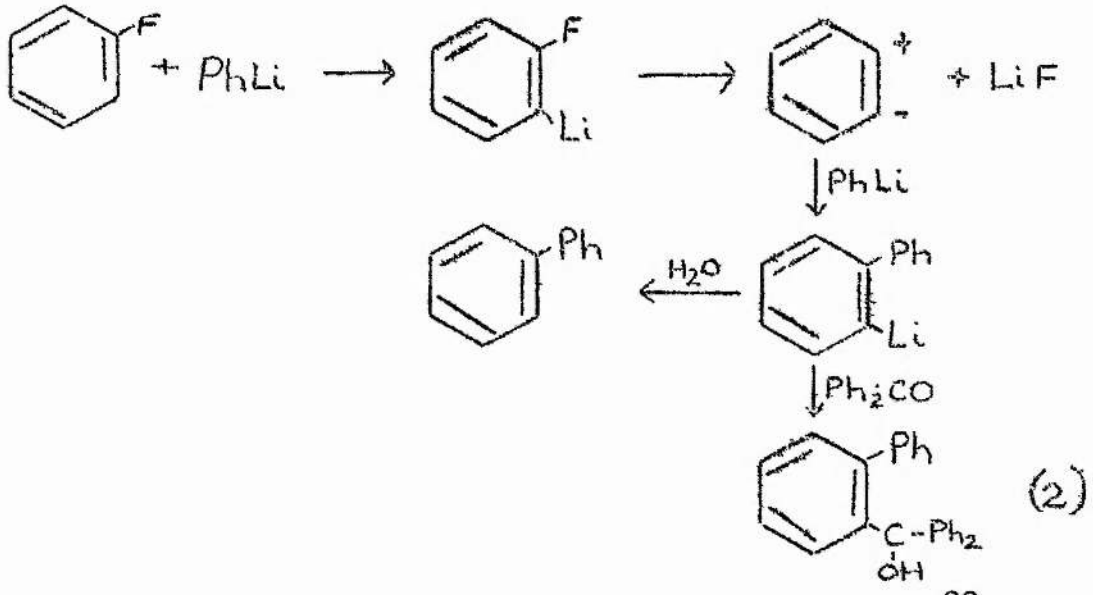

In this connection, the use of nitrosobenzanilides was considered to be advantageous experimentally as a result of the ease of isolation of the corresponding benzoic acid, which would crystallise directly from solution in carbon tetrachloride, for example.

Most of the work on N-nitroso compounds described above has been carried out using nitrosoacetanilides, and very little has been done with nitrosobenzanilides. Although Suschitzky used benzanilides to demonstrate the existence of ion pairs, and Kampmeier and Rubin studied o-iodo-N-nitrosobenzanilides, a systematic survey of the reactions of N-nitrosobenzanilides in various solvents had never been undertaken prior to this investigation now recorded in this thesis.

## 4. ARYNE INTERMEDIATES.

Although benzyne, or dehydrobenzene, ($C_6H_4$) had been proposed by early workers[84] as a transient intermediate in reactions of aromatic compounds, it was not until 1942 that it became generally accepted.[85] In reactions of aryl halides with phenyllithium, Wittig[85,86] found that aryl fluorides reacted much faster than the other aryl halides, and the products of the

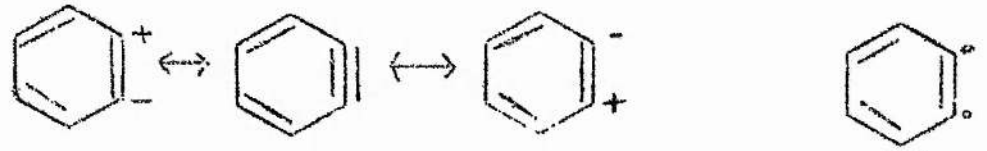
reaction depended on the subsequent treatment of the reaction mixture. Addition of water gave biphenyl, while o-biphenyldiphenylcarbinol (2) was obtained by the addition of benzophenone. Since it had been shown[87] that ω-chlorostyrene reacted with phenyllithium to give an acetylenic derivative, presumably by substitution of the metal in the β-position, followed by elimination of the metal halide, Wittig[85] proposed the following scheme:




(2)

The isolation of o-fluorophenyllithium by later workers.[88] supported this scheme.

Wittig postulated that the intermediate was permanently polarised in one sense, as shown. However, isolation of isomeric mixtures of products in other reactions[91] (see p. 21 ), showed that it was capable of existence in various canonical forms:

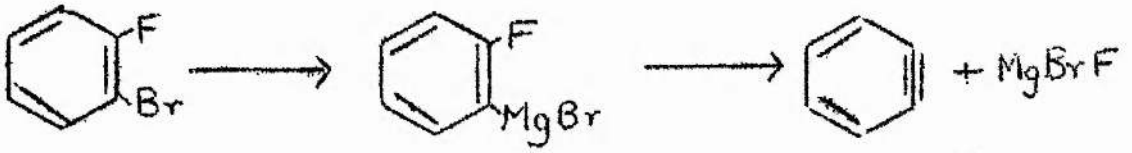
i.e. 

(3)

A contribution from the diradical structure (3) was also considered.[124]

The speed of the reaction was attributed to the strong electronegativity of the fluorine which enabled the o-hydrogen to be replaced by the metal. Lithium fluoride was then eliminated by the combined effects of the electropositive metal and electronegative fluorine.[94] Other halogens, being less electronegative, reacted less readily.

The reaction of o-dihalogenobenzenes with lithium was shown to proceed by a similar route after initial displacement of one halogen by the metal.[88,95,97] Arynes have also been generated by the reaction of Grignard reagents formed from these aryl halides.[95]

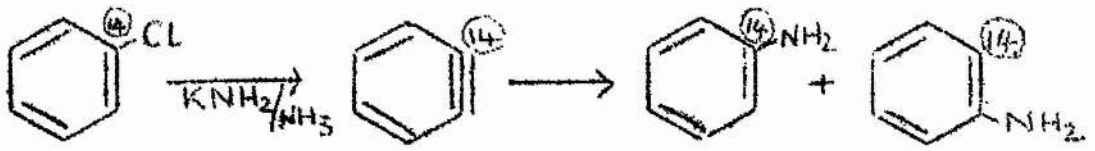



Results from reactions of halogenated naphthalenes[98] paralleled those from halogenated benzenes.

Further methods for the generation of arynes include the following:

a) Amination of Aryl Halides with Metallic Amides.

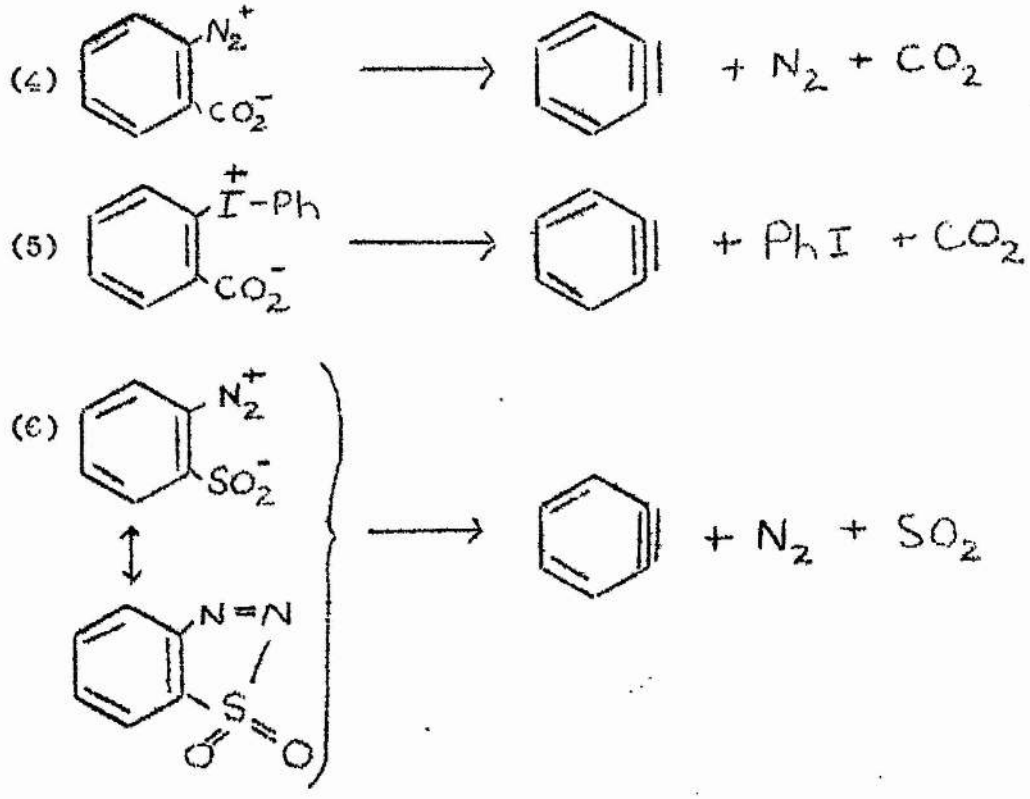
To explain the mixture of products from the reaction of substituted aryl halides with metallic amides,[89,90,91,92] Roberts et al.[91] proposed an intermediate aryne. Compelling evidence came from their reactions with 1-$C^{14}$-chlorobenzene, where there was formed a mixture of products, the ratio being as predicted, taking into account the isotope effect.



Similar results were obtained in reactions of halogenated naphthalenes.[93]

b) Decomposition of Benzenediazonium-2-carboxylate[99] (4) diphenyliodonium-2-carboxylate[100-102] (5) and diazotised o-aminobenzenesulphinic acid.[103] (6)

Thermal decomposition of these compounds was shown to yield benzyne by elimination of the two o-substituents as complete molecules.

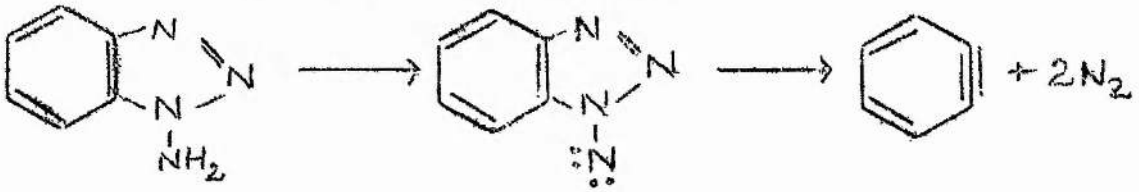


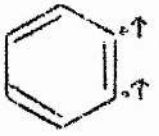
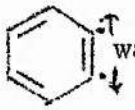
The presence of the aryne was indicated by trapping experiments (see later, p. 24).

A modification of this type of reaction, the formation of benzenediazonium-2-carboxylate in situ by diazotisation of anthranilic acid with amyl nitrite, has been found to be a convenient method of generating benzyne in aprotic solvents.[100]

c) Oxidation of 1-Aminobenzotriazole.

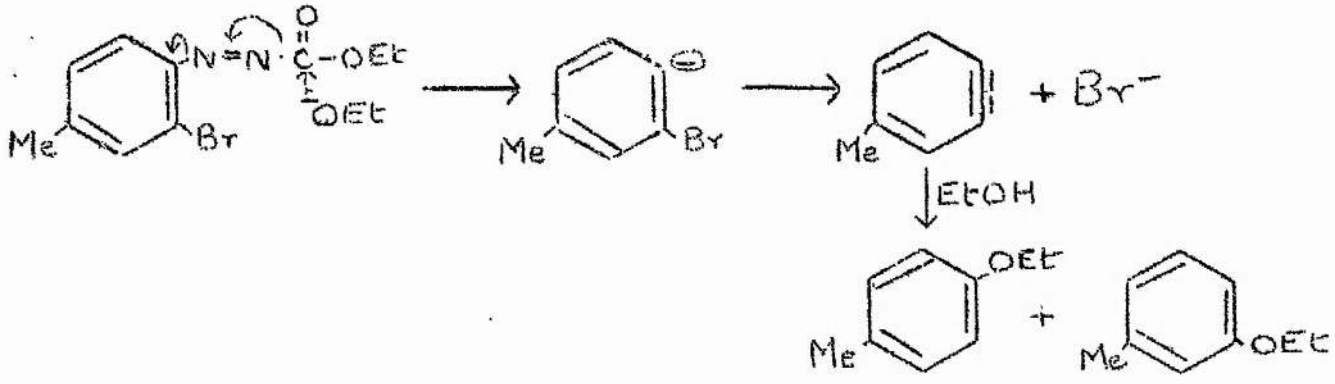
Oxidation of 1-aminobenzotriazole with lead tetra-acetate gave rise to benzyne, possibly via an intermediate nitrene.[104]



Oxidation of 2-aminobenzotriazole also yielded benzyne, but it readily dimerised, even in the presence of aryne traps, whereas benzyne from previous sources did not. It has been suggested that the triplet state  and not the usual singlet state  was present in this case.

d) The decomposition of diazo compounds with base.

The action of sodium ethoxide on an o-bromo diazo compound gave rise to an intermediate benzyne.[106]

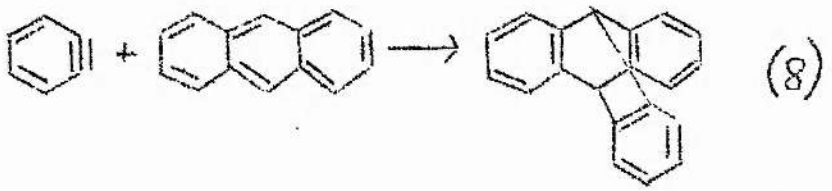


## 2. REACTIONS OF ARYNES.

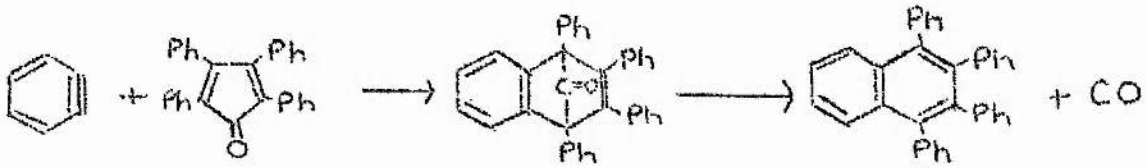
### A. Reaction with Dienes.

The reaction of a benzyne intermediate with cyclic dienes proved to be the most important diagnostic test for its presence in a reaction. The dienes most commonly used as traps for benzyne were furan[94,95,103,104,109] with which it gave 1,4-epoxy-1,4-dihydronaphthalene (7), anthracene[94,95,100,103,104,109] which yielded triptycene (8), and 2,3,4,5-tetraphenylcyclopentadienone[95,100,104,107,108] which gave 1,2,3,4-tetraphenylnaphthalene (9).

i.e.  (7) and no phenyl furan.[94,95]



(8)



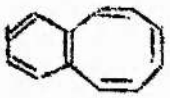
(9)

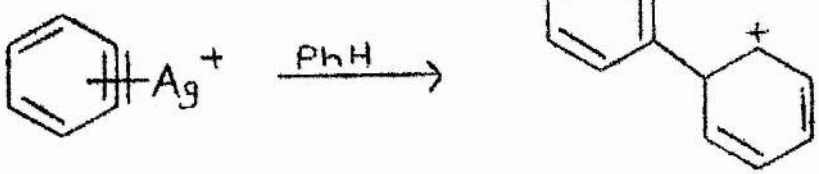
Cyclopentadiene,[94,95] tetraphenylfuran[95] and pyrroles[111] have also been used as traps.

The addition reaction was found to be favoured by a high electron density in the diene and also by electron withdrawing groups in the aryne.[102,110] Thus, anthracene was much less efficient as a trap than 2,5-di-p-anisyl-3,4-diphenylcyclopentadienone.

B. Reactions with benzene and substituted benzenes.

Originally, aromatic compounds such as benzene were thought to have a low reactivity towards benzyne, but close examination showed that, in some cases, small quantities of addition products were formed.[113]

Benzyne from benzenediazonium-2-carboxylate in benzene yielded benzobicyclo(2,2,2)-octatriene [  ] by 1,4-addition, benzocyclo-octatetraene [  ] by 1,2-addition followed by valence bond isomerism, and biphenyl by insertion of the benzyne into a C-H bond in benzene.[113] Benzyne produced from other reactions,[114,115] e.g. amyl nitrite and anthranilic acid, however, gave benzobicyclo(2,2,2)-octatriene and biphenylene, and only very small quantities of biphenyl and benzocyclo-octatetraene. The difference in these reactions was explained by Friedman,[114] who suggested that, as the preparation of benzenediazonium-2-carboxylate was carried out in the presence of silver ions, contamination might result, and a benzyne-silver complex could be formed. This would be more electrophilic than benzyne and would attack benzene.

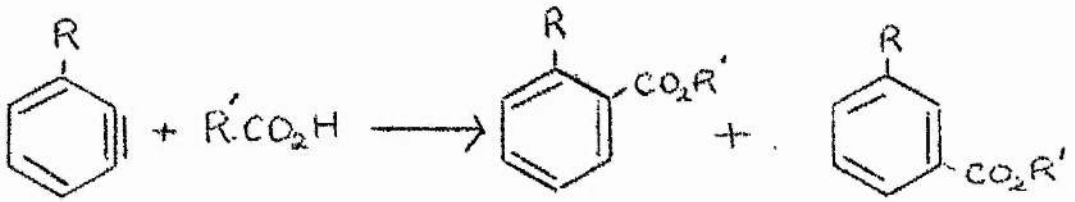
i.e. 


By intra- or intermolecular proton transfer and ejection of $Ag^+$, biphenyl

would be formed. Benzocyclo-octatetraene formation was explained by ring closure and valence bond isomerism. This explanation was substantiated by producing benzyne from anthranilic acid diazotised with amyl nitrite in the presence of added silver ions, when there was an increase in the yield of biphenyl and benzocyclo-octatetraene and a corresponding decrease in the yield of benzobicyclo(2,2,2)-octatriene. No other metal ion has so far been shown to have a similar effect. By the use of substituted benzenes,[11f] it was possible to show preference for 1,4-addition rather than 1,2-addition, and to show that benzyne tended to avoid adding to carbon atoms bearing a substituent.

C. Reaction with Carboxylic Acids.

A mixture of esters resulted from the reaction of an asymmetric aryne with a carboxylic acid.[117]

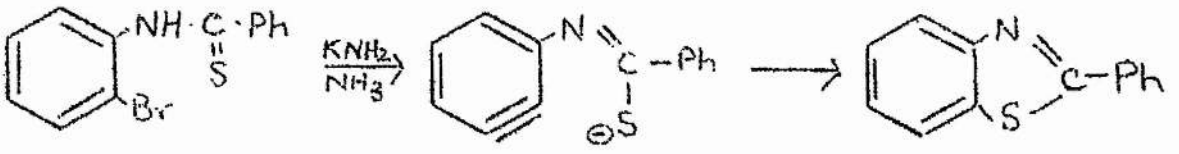



D. Other Reactions.

Benzyne has been shown to react with phenylacetylenes,[112a] tertiary bases,[94c,112] thio ethers,[118] ketones[119] and allylic olefins.[120]

The reaction of ring closure via an aryne intermediate is useful in synthetic work for the production of polycyclic compounds.[121]

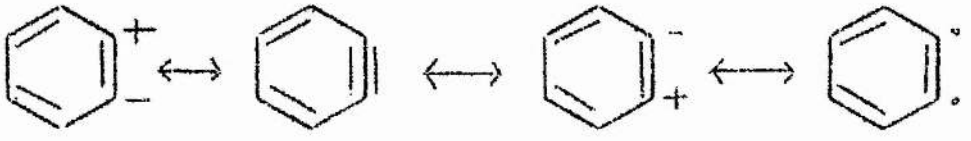
e.g.



The orientation of addition to the triple bond in substituted arynes has been studied by various workers[91c,124,125] and it has been shown to depend on both the inductive and the conjugative effects of the substituent for both 3- and 4-substituted arynes.

3. Structural Considerations.

From its reactions, the benzyne intermediate would appear to exist in a triply bonded, dipolar or diradical form.



(10) (11) (12) (13)

In structure (11), one electron resides in each of the two adjacent $sp^2$ orbitals, and there is a certain amount of overlap. Owing to ring strain, the overlap will, however, be only slight in comparison with that in acyclic acetylenes, and the compound (11) will have enhanced reactivity as a dienophile.[122] The relative weakness of this bond explains the susceptibility to attack by nucleophiles e.g. $Ph^-$, which intercept the dehydrobenzene as o-lithiobiphenyl.

The two electrons with antiparallel spins may reside in one $sp^2$ orbital, giving rise to the limiting dipolar forms (10) and (12).

Wittig[85] had suggested that the bond was permanently polarised in only one sense, but isolation of mixtures of isomers disproved his theory.

The triplet state (diradical) may also be present in the resonance hybrid.[124] There are few products isolated which are indicative solely of radical intermediates, but such a structure was proposed to account for the production of triphenylene in the reaction of fluorobenzene with phenyl lithium.[97,108] This has, however, also been attributed to an ionic mechanism.

# EXPERIMENTAL

Page

## ABBREVIATIONS

| | | |
|---|---|---|
| G.L.C. | - | gas-liquid chromatography |
| I.R. | - | infra red |
| U.V. | - | ultra violet |
| N.M.R. | - | nuclear magnetic resonance |
| E.S.R. | - | electron spin resonance |
| m.p. | - | melting point |
| b.p. | - | boiling point |
| m/m | - | moles of product per mole of starting material. |

# EXPERIMENTAL

## I. ANALYTICAL INSTRUMENTS

### 1. Gas-Liquid Chromatographs

The instrument used for qualitative work was a Perkin-Elmer model F.11, employing nitrogen as the carrier gas and fitted with a flame-ionisation detector. The columns used were in the form of coils, 2 metres long and 1/8" in diameter. A second instrument was used for both qualitative and quantitative work. This, a Griffin and George model D. 6., also used nitrogen as the carrier gas, but was fitted with a gas-density balance. The columns used were 2 metres long and 3/16" in diameter. All qualitative analyses were checked on at least two columns, compounds being identified by retention time and also by showing peak enhancement in mixtures of the unknown with authentic compounds. The quantitative analyses were carried out using an internal standard technique. After a standard of suitable retention time had been found, a known weight of it was added to the reaction mixture in approximately the same concentration as the reaction products. The amounts of the various constituents present were then computed from the relative areas of the peaks, since the area of the peak traced out on the recorder is directly proportional to the molecular weight, as shown by the equation:

$$n = \frac{kA}{M - m},$$

where $n$ = no. of moles of product

$m$ = molecular weight of carrier gas

$A$ = area of peak

$M$ = molecular weight of product

$k$ = constant

For two compounds, $\frac{n_1}{n_2} = \frac{A_1}{A_2} \times \frac{(M_2 - m)}{(M_1 - m)}$

For preparative work, an Aerograph Autoprep Model A-700 with 3/8" diameter columns, 8' long, fitted with a flame ionisation detector, and employing nitrogen as the carrier gas, was used.

Abbreviations for columns used:-

PEGA - polyethylene glycol adipate
SIL - silicone oil
NPGS - neopentyl glycol succinate
CAR - carbowax

} on 100 - 120 mesh celite

APL - apiezon "L" grease - on 100-120 mesh silocel.

2. N.M.R. Spectrometer

A Perkin-Elmer Nuclear Magnetic Resonance Spectrometer, Model R-10, with probe temperature 33.5°C and operating at 60 Mc/sec. was used for all proton resonance spectra.

3. I.R. Spectrometers

The various spectrometers used were (i) Grubb-Parsons, Type 9.S.2A, (ii) a Perkin-Elmer model 137 and (iii) a Perkin-Elmer model 237. Solids were examined as nujol mulls, and liquids as thin films.

4. U.V. Spectrometer

A Unicam S.P-800 model was used for all ultraviolet spectra.

5. Melting points were recorded on a Kofler hot-stage apparatus.

6. Thin Layer Chromatography All plates used were coated with either silica gel or alumina, and were developed by iodine, except when one of the compounds was tetraphenylnaphthalene, when the spots were viewed under U.V. light.

## II. PREPARATION AND PURIFICATION OF MATERIALS

### A Solvents

i) Carbon tetrachloride was dried over calcium chloride, and then fractionally distilled through a 50 x 2 cm. helix-packed column. The pure solvent had b.p. 76.5°, and contained no trace of impurity when examined by G.L.C. A trace of chloroform would have been detected by this method. The pure carbon tetrachloride was stored over molecular sieve.

ii) Benzene was distilled, dried over sodium wire, and then redistilled, the middle fraction being retained. No impurity was shown by G.L.C. analysis. The pure product was stored over sodium wire, and had b.p. 80°.

B Acid Chlorides

The preparation of the acid chlorides is exemplified by the preparation of p-chlorobenzoyl chloride.

p-Chlorobenzoic acid (50 g., 0.32 mole) was boiled under reflux with thionyl chloride (75 ml., 0.96 mole) until the solution was clear, and until the evolution of acidic fumes had ceased (8 hours). The excess of thionyl chloride was removed by distillation, the last traces being removed as the azeotrope with benzene. Further distillation gave p-chlorobenzoyl chloride (43 g., 85%), b.p. 100°/10 mm., (lit.[126] 120°/22 mm.) .

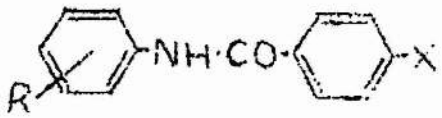
The following acyl chlorides were prepared by the above method:

| acyl chloride | yield (%) | b.p.° | lit. b.p.° | |
|---|---|---|---|---|
| 4-bromobenzoyl chloride | 84 | 94/0.1mm. | 133/17 mm. | [127] |
| 4-chlorobenzoyl chloride | 85 | 100/10mm. | 120/22 mm. | [126] |
| 4-methylbenzoyl chloride | 82 | 34/8mm. | 125/35mm. | [128] |

4-Bromobenzoyl chloride had m.p. 42°.

TABLE 1

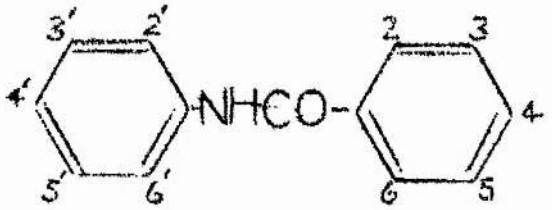
Preparation of Benzanilides by Schotten-Baumann Method




| R | X | Yield (%) | m.p. °C | lit. m.p. °C | Analysis |
|---|---|---|---|---|---|
| H | 4-Cl | 72 | 195 | 192-194 [129] | - |
| 2'-Br | 4-Cl | 68 | 137-138 | - | Found: C, 50.2; H, 3.2%<br>$C_{13}H_9BrClNO$ requires<br>C, 50.3; H, 2.9% |
| 3'-Br | 4-Cl | 73 | 127 | - | Found: C, 50.1; H, 3.0%<br>$C_{13}H_9BrClNO$ requires<br>C, 50.3; H, 2.9% |
| 4'-Br | 4-Cl | 56 | 215-216 | - | Found: C, 50.5; H, 3.1%<br>$C_{13}H_9BrClNO$ requires<br>C, 50.3; H, 2.9% |
| 3'-Me | 4-Cl | 55 | 127-128 | - | Found: C, 68.5; H, 4.7%<br>$C_{14}H_{12}ClNO$ requires<br>C, 68.4; H, 4.9% |
| 4'-Me | 4-Cl | 65 | 211 | 212-213 [130] | |
| H | 4-Me | 60 | 144 | 144-145 [123] | |
| H | 4-$NO_2$ | 50 | 208-210 | 211 [131] | |

C Benzanilides

The system of nomenclature is based on the following structure:*




The methods used in the preparation of benzanilides are given below. In all cases, the I.R. spectrum of the prepared compounds showed absorption in the ranges 1640-1700 cm.$^{-1}$ (>C=O) and 3200-3420 cm.$^{-1}$ (>N-H).

i) The following benzanilides were prepared by the Schotten-Baumann method [155], and recrystallised from ethanol. (See Table 1 opposite).

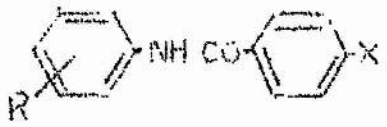
ii) The second method of preparation is exemplified by the preparation of 4-chloro-4'-nitrobenzanilide.

4-Nitroaniline (13.8 g., 0.1 mole) and 4-chlorobenzoyl chloride (17.5 g., 0.1 mole) in pyridine (60 ml.) were boiled under reflux for 8 hours. The solution was cooled, and poured into hydrochloric acid (2N, 600 ml.). The resultant precipitate was washed free from acid, and recrystallised from ethanol to give 4-chloro-4'-nitrobenzanilide (23.5 g., 35%), m.p. 221-222° (lit. [132] 222°). Also prepared by this method were the following (See Table 2, overleaf)

* This is the numbering used in Chemical Abstracts.

TABLE 2

Preparation of Substituted Benzanilides




| R | X | Yield (%) | m.p.° | lit. m.p.° | Analysis |
|---|---|---|---|---|---|
| 4'-$NO_2$ | 4-Br | 88 | 242-243 | 243-244 [133] | - |
| 3'-$NO_2$ | 4-Cl | 70 | 188-190 | 187 [134] | Found: C, 56.3; H, 3.3% Calc. for $C_{13}H_9ClN_2O_3$; C, 56.5; H, 3.3% |
| 2',4',6' triBr | 4-Cl | 58 | 211-212 | - | Found: C, 33.1; H, 1.6% $C_{13}H_7Br_3ClNO$ requires C, 33.3; H, 1.5% |
| 4'-Br | 4-Br | 88 | 220 | 222 [135] | |
| 2',6'-diCl | 4-Cl | 78 | 194-195 | - | Found: C, 51.6; H,2.6; N, 5.0%. $C_{13}H_3Cl_3NO$ requires C, 51.9; H, 2.7; N, 4.7%. |

NOTE:- 4-Bromo-4'-nitrobenzanilide was recrystallised from a mixture of 75% ethanol + 25% acetic acid. 4-Chloro-2',4',6'-tribromobenzanilide was recrystallised from benzene.

D N-Nitrosoacylarylamines

(i) N-Nitrosoacetanilide

N-Nitrosoacetanilide was prepared by a modified form of the method of Hey et al [50(a)].

A suspension of acetanilide (5 g.) in a mixture of acetic acid (35 ml.) and acetic anhydride (15 ml.) containing potassium acetate (5 g.) and phosphorus pentoxide (0.5 g.) was magnetically stirred at 5°. Nitrosyl chloride [136] (3 g.) in acetic anhydride (30 ml.) was added dropwise over 20 min. The mixture was stirred a further 30 min., and then poured into ice-water (1 l.). The nitroso-acetanilide separated as a yellow, crystalline solid. This was thoroughly washed with cold water and dried between filter papers. Final drying was carried out over phosphorus pentoxide at 0.05 mm. for 3 hours at room temperature. N-Nitrosoacetanilide (4.3 g., 75%) had m.p. 51-52° (decomp.), (lit.[50(a)] 52-53°). The compound was not recrystallised due to the risk of decomposition.

Similarly prepared was 4-chloro-N-nitrosoacetanilide, m.p. 73° (decomp.), (lit. [137] 83-84°).

(ii) N-Nitrosobenzanilides

Attempts to nitrosate benzanilides on a large scale by the above procedure resulted in only partial nitrosation. Only 4-chloro-benzanilide and 4-chloro-4'-methylbenzanilide were successfully nitrosated by this method. The general method used for nitrosation of benzanilides was similar to that used by Miles and Suschitzky [73], and it is illustrated by the preparation of 4-chloro-N-nitrosobenzanilide.

A mixture of 4-chlorobenzanilide (10 g.), acetic acid (100 ml.), acetic anhydride (100 ml.), and pyridine (30 ml.) was magnetically stirred and cooled to $0^{\circ}$. Nitrosyl chloride (20 g.) in acetic anhydride (100 ml.) was added dropwise over 30 min., stirring was continued for a further 15 min., and the mixture was poured into ice-water. Washing and drying were carried out as in the method described for the preparation of nitrosoacetanilide. The product (7.7 g., 60%) had m.p. $75^{\circ}$ (violent decomposition).

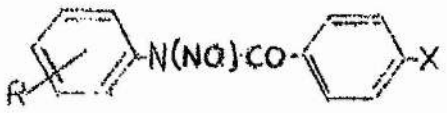
The following N-nitrosobenzanilides were prepared by this method: (See Table 3, p. 44).

No recrystallisation of any of the nitroso compounds was attempted due to the risk of explosion or decomposition. The dry compounds were treated with great care.

Complete nitrosation was shown in each case by the absence of absorption in the >N-H region of the I.R. spectrum (3200-2420 $cm.^{-1}$) and also by a shift in the carbonyl frequency from that of the parent benzanilide (1640-1700 $cm.^{-1}$) to the range 1670-1720 $cm.^{-1}$. The yields of product were always less than 100% owing to the solubility of the product in the aqueous solution.

TABLE 3

Preparation of N-Nitrosobenzanilides




| R | X | Yield (%) | m.p. | |
|---|---|---|---|---|
| 3-Br | 4-Cl | 69 | 57 | (decomp.) |
| 4-Br | 4-Cl | 59 | 71 | (decomp.) |
| 4-$NO_2$ | 4-Br | 64 | 73 | (decomp.) |
| 3-Me | 4-Cl | 58 | 65 | (decomp.) |
| 4-Me | 4-Cl | 60 | 60 | (decomp.) |
| 3-$NO_2$ | 4-Cl | 78 | 81 | (decomp.) |
| 4-$NO_2$ | 4-Cl | 84 | 86 | (decomp.) |
| 2-Br | 4-Cl | 82 | 68 | (decomp.) |
| 2,4,6-triBr | 4-Cl | 80 | 95 | |
| 4-Br | 4-Br | 75 | 80 | (decomp.) |
| 2,6-diCl | 4-Cl | 90 | 67 | |
| H | 4-Me | 20 | 62 | (decomp.) |
| H | 4-$NO_2$ | 58 | 79 | (decomp.) |

E Phenols

i) 2,3,5-Tribromophenol

A solution of o-anisidine (25 g.) in acetic acid (60 ml.) was stirred and cooled to 0° while bromine (84 g.) was added dropwise. The resulting solid was filtered off and suspended in acetic acid. Bromine (48 g.) was added and the mixture was boiled under reflux for 2 hours, and then allowed to cool. The precipitate was recrystallised from ethanol, giving 2-methoxy-3,4,6-tribromoaniline (23.8 g.), m.p. 97-99° (lit.[138] 102°).

A solution of 2-methoxy-3,4,6-tribromoaniline (23.0 g.) in ethanol (134 ml.) was treated with concentrated sulphuric acid (13 ml.) in small portions, the whole being stirred and cooled so that the temperature did not exceed 20°. Sodium nitrite (5.2 g.) was then added in small portions over 1 hr. The mixture was boiled under reflux for 1½ hrs. to decompose the diazo compound, and poured into water. The precipitate was recrystallised from ethanol, giving yellow crystals of 2,3,5-tribromoanisole (13 g.), m.p. 76-78° (lit.[138] 82°).

To a solution of the tribromoanisole (5 g.) in acetic acid (20 ml.) was added dropwise hydrobromic acid (60%, 10 ml.) and the mixture was boiled under reflux for 4 hrs., during which hydrobromic acid (5 ml.) was added every ½ hr. A white precipitate was obtained by pouring the cooled reaction mixture into water. The solid was dissolved in hot potassium hydroxide solution, and the phenol precipitated by adding sulphuric acid (20%). Recrystallisation from light

petroleum (b.p. 40-60°) gave 2,3,5-tribromophenol (2.1 g., 48%) m.p. 92° (lit.[133] 95°). G.L.C. analysis showed that this phenol contained no impurities. The N.M.R. spectrum was consistent with 2,3,5-tribromophenol, showing absorptions at $\tau$ = 4.38(-OH) and two doublets (2 H), centres at $\tau$ = 2.60 and 2.8, with J = 2.2 c/s.

(ii) 2-Chloro-3,5-dibromophenol.[139]

Bromine (.40 ml.) was added dropwise to o-chlorophenol (25 g.), containing a pinch of iron powder. The reaction mixture was allowed to stand overnight, and then the excess bromine was driven off by heating on a water-bath. Dilute hydrochloric acid (1:1, 200 ml.) was added, and heating was continued for a further 2 hrs. until the iron salts had dissolved. The remaining solid was recrystallised from ethanol, giving cream-coloured needles, 2-chloro-3,4,5,6-tetrabromophenol (66 g., 32%), m.p. 220-221° (lit.[139] 222°). The N.M.R. spectrum showed the absence of aromatic protons, i.e. the compound was fully brominated.

The 2-chloro-3,4,5,6-tetrabromophenol (34 g.) and aluminium chloride (59.5 g.) were boiled under reflux with benzene (85 ml.) for 4 hours, until the mixture became very dark and the evolution of white fumes had ceased. The mixture was poured on to ice, and concentrated hydrochloric acid was added so that the mixture was strongly acidic. Extraction with ether gave a solid, which was dissolved in an excess of light petroleum (b.p. 40-60°), and extracted with potassium hydroxide (2N). Acidification of this alkaline extract yielded a white solid, recrystallisation of which from light petroleum (b.p. 40-60°) gave

2-chloro-3,5-dibromophenol (12.8 g., 58%), m.p. 63-65° (lit.[139] 66°). The I.R. and N.M.R. spectra were in accordance with this structure, the latter showing absorptions at $\tau$ = 4.37 (-OH) and two doublets (2 H), centres $\tau$ = 2.62 and 2.8, with J = 2.2 c/s. G.L.C. analysis showed that the compound was pure.

(iii) 2,4,6-Tribromophenol[140]

Bromine was added dropwise to a stirred solution of phenol (5 g.) in water, until the solution acquired a permanent yellow colour. The white solid formed was recrystallised from light petroleum (b.p. 40-60°), giving 2,4,6-tribromophenol (8.4 g., 50%), m.p. 92° (lit.[140] 95°).

(iv) 4-Chloro-2,6-dibromophenol[141]

Bromine (12.8 g.) in acetic acid (25 ml.) was added dropwise to a stirred solution of p-chlorophenol (5.14 g.) in acetic acid (25 ml.). Water was added, giving a white precipitate, which was recrystallised from ethanol to give white needles (6.8 g., 61%), m.p. 89-90° (lit.[141] 90°). The I.R. spectrum was in accordance with this structure.

(v) 2-Chloro-4,6-dibromophenol[142]

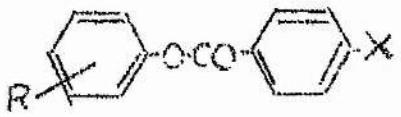
o-Chlorophenol (2.6 g.) was dissolved in a mixture of acetic acid (15 ml.) and water (15 ml.). To the stirred solution was added dropwise bromine (6 g.) in acetic acid (10 ml.). The white precipitate was recrystallised from ethanol, giving 2-chloro-4,6-dibromophenol (4.9 g., 85%), m.p. 74-76° (lit.[142] 76°).

F Esters

(i) The following esters were prepared by the Schotten-Baumann method:[155] (See Table 4).

TABLE 4

Preparation of Esters by Schotten-Baumann Method



| R | X | Yield (%) | m.p.° | lit. m.p.° | Analysis |
|---|---|---|---|---|---|
| 3-Br | 4-Cl | 50 | 96-97 | - | Found: C, 49.8; H, 2.3. $C_{13}H_8BrClO_2$ requires C, 50.1; H, 2.6% |
| 4-Br | 4-Cl | 50 | 105-106 | - | Found: C, 50.3; H, 3.0. $C_{13}H_8BrClO_2$ requires C, 50.1; H, 2.6% |
| 4-Cl | 4-Cl | 65 | 95-96 | 96 [144] | |
| 4-Me | 4-Cl | 75 | 98-100 | 97-98 [144] | |
| H | 4-Cl | 55 | 103-104 | 101-102 [143] | |
| H | 4-Me | 59 | 73-75 | 71-72 [144] | |
| 2,3-DiCl | 4-Cl | 55 | 120-122 | - | Found: C, 51.7; H, 2.4. $C_{13}H_7Cl_3O_2$ requires C, 51.8; H, 2.3% |
| 2,4,6-TriBr | 4-Cl | 43 | 96 | - | Found: C, 33.4; H, 1.3. $C_{13}H_6Br_3ClO_2$ requires C, 33.3; H, 1.3% |

TABLE 4 cont.

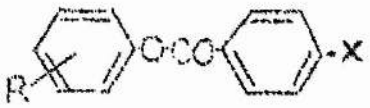
| R | X | Yield (%) | m.p.° | lit. m.p.° | Analysis |
|---|---|---|---|---|---|
| 3-Me | 4-Cl | 67 | 92-94 | 100-101[143] | |
| 4-Cl-2,6-diBr | 4-Cl | 35 | 66 | - | Found: C, 36.9; H, 1.7. $C_{13}H_6Br_2Cl_2O_2$ requires C, 36.7; H, 1.4% |
| 2-Cl-4,6-diBr | 4-Cl | 50 | 90-93 | - | Found: C, 36.4; H, 1.5. $C_{13}H_6Br_2Cl_2O_2$ requires C, 36.7; H, 1.4% |
| 2-Cl-3,5-diBr | 4-Cl | 60 | 172 | - | Found: C, 36.5; H, 1.1. $C_{13}H_6Br_2Cl_2O_2$ requires C, 36.7; H, 1.4% |
| 2-Cl | 4-Cl | 52 | 59-60 | - | Found: C, 58.4; H, 3.3. $C_{13}H_8Cl_2O_2$ requires C, 58.2; H, 3.0% |
| 2-Br | 4-Cl | 64 | 74-75 | - | Found: C, 50.2; H, 2.8. $C_{13}H_8BrClO_2$ requires C, 50.0; H, 2.6% |

(ii) In the cases where the phenols are more strongly acidic, or in cases where the ester is otherwise difficult to prepare, the phenol and the acid chloride may react without the presence of a base. This method is illustrated by the preparation of 4-nitrophenyl 4-chlorobenzoate.

p-Chlorobenzoyl chloride (2.2 g.) and p-nitrophenol (2 g.) were warmed on a water-bath until the evolution of hydrogen chloride ceased, and the mixture became solid. Recrystallisation from methanol gave 4-nitrophenyl 4-chlorobenzoate (1.7 g., 46%), m.p. 136° (lit.[145] 138°).

The following esters were prepared in a similar manner: (See Table 5).

TABLE 5



| R | X | Yield (%) | m.p.° | lit. m.p.° | Analysis |
|---|---|---|---|---|---|
| 4-Br | 4-Br | 29 | 113 | 114-115 [144] | |
| 4-Cl | 4-Br | 33 | 101 | 102 [144] | |
| 3-$NO_2$ | 4-Cl | 70 | 135 | - | Found: C, 56.4; H, 3.1. $C_{13}H_8ClNO_4$ requires C, 56.2; H, 2.9% |

(iii) 2,6-Dichlorophenyl 4-Chlorobenzoate

2,6-Dichlorophenol (1 g.) and p-chlorobenzoyl chloride (1.1 g.) were dissolved in pyridine ( 25 ml.) and the mixture was boiled under reflux for 3 hours. After cooling, the solution was poured into an excess of hydrochloric acid. The product was recrystallised from methanol, giving the ester (1.1 g., 60%), m.p. 70.5° [Found: C, 51.9; H, 2.6. $C_{13}H_7Cl_3O_2$ requires C, 51.8; H, 2.3%].

(iv) Phenyl 4-nitrobenzoate [131]

p-Nitrobenzoic acid (2.5 g.), phenol (1.4 g.) and pyridine (12 g.) were stirred in an ice-bath while thionyl chloride (2 g.) was added dropwise. After 3 hours, the reaction mixture was diluted with water. The precipitate was washed with water and recrystallised from ethanol, giving pale yellow needles (1.3 g., 50%), m.p. 128-130° (lit. [131] 129°).

Satisfactory I.R. spectra, showing carbonyl absorption in the range 1720-1760 $cm.^{-1}$, were obtained from all the prepared compounds.

G Halogenobenzenes

(i) 1-Chloro-2,4,6-tribromobenzene [146]

A solution of 2,4,6-tribromoaniline (5 g.) in sulphuric acid (d = 1.84, 9.5 ml.) was treated with a solution of sodium nitrite (2 g.) in sulphuric acid (d = 1.84, 10 ml.) and the mixture was stirred into acetic acid (20 ml.), the whole being ice-cooled. After 45 min., a sample gave no precipitate with water, showing the absence of

undiazotised amine. This solution was rapidly stirred into one of cuprous chloride (5 g.) in hydrochloric acid (d = 1.18, 25 ml.). After the vigorous evolution of nitrogen had ceased, the mixture was gradually heated to boiling, cooled, and then diluted with water. The resultant solid was washed with hot dilute hydrochloric acid and then with water. Recrystallisation from ethanol gave needles (1.42 g., 27%), m.p. 87° (lit.[146] 91°). Further recrystallisation did not raise the melting point, but G.L.C. analysis showed that this compound contained no impurity.

(ii) 1,2,3,5-Tetrabromobenzene

The method was essentially the same as that given for the preparation of 1-chloro-2,4,6-tribromobenzene, cuprous bromide in hydrobromic acid being used in place of cuprous chloride in hydrochloric acid. The product had m.p. 95° (lit.[146] 98°).

H 3-Bromobiphenyl

A solution of amyl nitrite (11.7 g.) in benzene (30 ml.) was boiled under reflux while a mixture of m-bromoaniline (8.5 g.) in benzene (30 ml.) was added dropwise over 30 min. The mixture was then boiled under reflux for a further 1 hour. The solvent was evaporated, and the product (4.4 g., 38%) distilled at 108°/0.15 mm. (lit.[147] 169°/17 mm.). [Found: C, 61.6; H, 3.7. Calc. for $C_{12}H_9Br$: C, 61.9; H, 3.9%]. The I.R. and N.M.R. spectra were consistent with the above structure, the latter spectrum showing only a complex multiplet at $\tau \approx 2.3$-$3.0$.

I Benzyne Traps

i) Anthracene

Commercial anthracene was purified by co-distillation with ethylene glycol.

ii) Furan

After distillation, the furan was stored over molecular sieve.

iii) 2,3,4,5-Tetraphenylcyclopentadienone

Benzil (5 g.) and dibenzyl ketone (5 g.) were heated in ethanol (50 ml.) until the solution almost boiled. A solution of potassium hydroxide (0.5 g.) in ethanol (5 ml.) was added slowly, and the mixture was then boiled under reflux for 10 min. After being cooled in ice, the mixture deposited dark-coloured crystals. Recrystallisation from a mixture of benzene/ethanol (1:1) gave dark purple crystals (9 g., 91%), m.p. 222°, lit.[140] 224°. A satisfactory I.R. spectrum was obtained.

J Benzyne Adducts

i) 1,4-Dihydronaphthalene-1,4-endoxide

A mixture of amyl nitrite (9.25 g.) and furan (9 g.) in methylene chloride (150 ml.) was boiled under reflux, while a solution of anthranilic acid (10 g.) in acetone (55 ml.) was added dropwise over 2 hours. The solvent was removed by distillation, and the product distilled at 68-73°/0.05 mm. Recrystallisation from

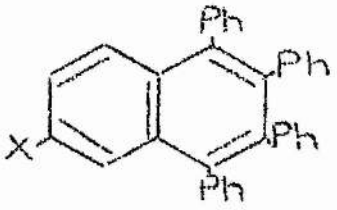
light petroleum (b.p. 60-80°) gave white crystals of the adduct (0.38 g., 4%) m.p. 55°, mixed m.p. 55-56°, (lit.[101] 55-56°). The I.R. spectrum of this compound was identical with that of an authentic sample.

ii) 1,2,3,4-Tetraphenylnaphthalene

A mixture of tetraphenylcyclopentadienone (11 g.) and amyl nitrite (3.8 g.) in methylene chloride (80 ml.) was boiled under reflux, while a solution of anthranilic acid (4 g.) in acetone (22.5 ml.) was added dropwise over 1 hour. The solvent was removed, and the dark solid was chromatographed on alumina. Elution with a mixture of light petroleum (b.p. 40-60°)/benzene (4:1) gave a white solid which, when recrystallised from acetic acid, gave 1,2,3,4-tetraphenylnaphthalene (7.2 g., 54%), m.p. 199° (lit.[95] 204°). Further recrystallisation did not raise the m.p. The I.R. spectrum was in accordance with this structure. The N.M.R. spectrum showed two phenyl resonances at 3.22τ(10 H) and 2.83 τ (10 H) due to the β-and the α-phenyl groups respectively. All the protons on any one phenyl group have almost the same chemical shift, giving rise to broad singlets. There is also an AA'BB' spectrum typical of an o-disubstituted benzene, with A- resonances ca 2.4 τ and B resonances ca 2.7 τ.

Also prepared by the above method, using the appropriate anthranilic acids, were the following. (See Table 6).

TABLE 6

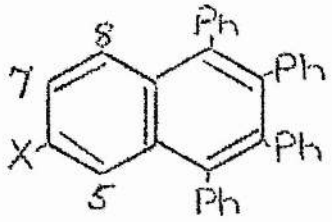



| X | Yield (%) | m.p.° | lit. m.p.° | Analysis |
|---|---|---|---|---|
| Br | 80 | 243-244 | - | Found: C, 80.2, H, 4.8. $C_{34}H_{23}Br$ requires C, 79.9; H, 4.5% |
| Me | 70 | 223 | 222 [104] | Found: C, 93.8; H, 5.9. Calc. for $C_{35}H_{26}$; C, 94.1; H, 5.9% |

The 6-methyl adduct had mixed m.p. of 223° with an authentic sample (m.p. 223°) supplied by Professor C.W. Rees.

The I.R. spectra were in accordance with these structures.

The N.M.R. spectra are detailed below.




| X | Absorption (τ) | Nature of Absorption | J(c/s) | Proton Responsible for Absorption |
|---|---|---|---|---|
| Br | 3.24 | broad singlet (10 H) | - | β-phenyl |
| | 2.33 | broad singlet (10 H) | - | α-phenyl |
| | 2.7 | double doublet (1 H) | 8.2, 1.8 | $H_7$ |
| | 2.49 | double doublet (1 H) | 8.2, 0.8 | possibly $H_8$ |
| | 2.31 | double doublet (1 H) | 1.8, 0.8 | possibly $H_5$ |
| Me | 7.6 | broad singlet (3 H) | - | methyl |
| | 3.2 | broad singlet (10 H) | - | β-phenyl |
| | 2.84 | double doublet (1 H) | 8.5, 2.0 | $H_7$ |
| | 2.83 | broad singlet (10 H) | - | α-phenyl |
| | 2.62 | double doublet (1 H) | 2.0, 0.8 | possibly $H_5$ |
| | 2.47 | double doublet (1 H) | 8.5, 0.8 | possibly $H_8$ |

iii) 5-Methyl-1,2,3,4-tetraphenylnaphthalene

A sample (m.p. 242-243°) for N.M.R. spectral studies was kindly supplied by Professor C.W. Rees. The spectrum showed a broad singlet at 8.01 τ (3 H) and three phenyl absorptions at τ = 3.18 (10 H) [β-phenyl groups] and τ = 2.84 (5 H) and 2.79 (5 H) [α-phenyl groups]. The absorption of the remaining aromatic protons could not be resolved due to the low concentration of the solution.

K 2-Amino-4-bromobenzoic acid

5-Bromoisatin (22.6 g.) was dissolved, by warming, in aqueous sodium hydroxide solution (12 g. in 300 ml.). Hydrogen peroxide (100 vol., 7.43 g.) was added in portions until oxidation was complete, as shown by the absence of the isatin colour on acidification of a portion of the reaction mixture. The solution was cooled, and almost neutralised with hydrochloric acid (1 N). It was then filtered through charcoal, giving a yellow solution, which, on careful acidification with dilute hydrochloric acid yielded a yellow solid. Recrystallisation from aqueous ethanol gavo yellow needles (6.4 g., 30%), m.p. 220° (lit.[149] 222°). The I.R. spectrum of this compound was consistant with 2-amino-4-bromobenzoic acid. [Found: C, 39.1; H, 3.0. Calc. for $C_7H_6BrNO_2$: C, 38.9; H, 2.8%].

## III REACTIONS OF N-NITROSOACYLARYLAMINES IN ORGANIC SOLVENTS

### A Decomposition of 4-Chloro-N-Nitrosobenzanilide in Chlorobenzene

4-Chloro-N-nitrosobenzanilide (3.08 g.) and chlorobenzene (26.5 g.) were stirred together at room temperature, the apparatus being protected by a drying tube. There was a vigorous evolution of nitrogen, and the mixture became very dark brown in colour. To ensure completion of the reaction, the mixture was boiled under reflux for 6 hours. p-Chlorobenzoic acid (1.30 g., 0.93 m/m.) m.p. and mixed m.p. 239-241° was removed. G.L.C. analysis of the solution (10% PEGA, .2% NPGS/140°) showed the presence of o, m, and p-chlorobiphenyl. The m and p isomers could not be separated on the D.6. G.L.C., but the combined yield of these was found to be 0.42 g. (0.19 m/m.) while the yield of the o-isomer was 0.62 g. (0.23 m/m.) Using a capillary column in the F. 11. G.L.C., the ratio of isomers was found to be o:m:p = 60:23:17.

The chlorobenzene was distilled off, and the isomeric mixture of biphenyls (0.94 g.) distilled from the residue (b.p. 65-80°/0.1 mm.). The I.R. spectrum of this mixture was identical with that of an authentic mixture.

No other products were isolated.

B Reactions of N-Nitroso acylarylamines in Benzene

1) Mono-Substituted 4-Chloro-N-Nitrosobenzanilides

a) General Procedure

The nitrosoacylarylamine was added to the solvent, and the mixture was stirred at room temperature overnight, the apparatus being protected from atmospheric moisture by a silica-gel guard tube. A feathery precipitate soon appeared in place of the amorphous nitroso compound. To ensure completion of the reaction, the mixture was then boiled under reflux for 6 hours and allowed to cool. A solid was precipitated in all cases. This, after recrystallisation from acetic acid, was shown by m.p., mixed m.p., and I.R. spectrum to be p-chlorobenzoic acid. After the removal of the bulk of the solvent by distillation, a further precipitate appeared, which was also shown to be p-chlorobenzoic acid. The remaining solution was distilled under reduced pressure, yielding, in all cases, the appropriate substituted biphenyl. The involatile residue was chromatographed on alumina.

b) 4-Chloro-N-Nitrosobenzanilide

The nitroso compound (3.6 g.) was allowed to decompose in benzene (175 ml.), yielding p-chlorobenzoic acid (1.9 g., 0.33 m/m.), m.p. and mixed m.p. 244-245°. Distillation of the solution gave the following fractions: (a) a colourless liquid (11.2 g.), b.p. 80°, (b) a yellow solid (0.39 g.), b.p. 130°/11 mm., (c) a yellow solid sublimate (0.06 g.), bath temp. 160°/0.03 mm., and (d) a residue (0.46 g.).

Fraction (a) was shown to be pure benzene by G.L.C. (2% NPGS, 10% SIL/170°).

Fraction (b) was recrystallised from light petroleum (b.p. 60-80°) giving biphenyl (0.82 g., 0.33 m/m.), m.p. and mixed m.p. 70-71°. The I.R. spectrum was identical with that of authentic biphenyl. G.L.C. analysis showed the absence of any impurities.

G.L.C. (2% NPGS., 10% SIL/170°) of fraction (c) showed only 1 peak, the retention time of which corresponded to that of phenyl 4-chlorobenzoate (20 mg.). Benzene was added to this fraction and the insoluble p-chlorobenzoic acid (30 mg.) filtered off. Chromatography of the solution, followed by recrystallisation of the product from methanol, gave phenyl 4-chlorobenzoate, m.p. and mixed m.p. 103-104°.

Chromatography of fraction (d) with light petroleum (b.p. 40-60°) gave a white solid. Recrystallisation from methanol gave phenyl 4-chlorobenzoate (10 mg.), m.p. 101-103°, mixed m.p. 102-103°. The total yield of ester produced in the reaction was 30 mg. (0.01 m/m.).

c) 4'-Bromo-4-Chloro-N-Nitrosobenzanilide

The nitroso compound (4.94 g.) was allowed to decompose in benzene (133 ml.). p-Chlorobenzoic acid (1.37 g., 0.80 m/m.), m.p. 239-241°, mixed m.p. 240-242°, was removed as previously described. Distillation of the solution gave the following fractions: (a) a colourless liquid (13.1 g.), b.p. 79.5-80.5°, (b) a colourless liquid (1.4 g.), b.p. 30°/12 mm., (c) a yellow solid (2.2 g.), b.p. 100°/3.5 mm., and (d) a residue (1.1 g.).

G.L.C. (10% PEGA, 10% SIL/100°) showed that fraction (a) was pure benzene, while fraction (b) was benzene containing a trace of bromobenzene (6 mg., 0.003 m/m.).

The I.R. spectrum of fraction (c) was identical with that of 4-bromobiphenyl. Recrystallisation from methanol gave 4-bromobiphenyl (1.72 g., 0.50 m/m.), m.p. and mixed m.p. 87-88°. G.L.C. (10% CAR, 10% SIL/190°) showed the absence of any impurity.

Fraction (d) was chromatographed on alumina. Elution with benzene/ether (1:1) gave 4'-bromo-4-chlorobenzanilide (0.12 g., 0.03 m/m.), m.p. and mixed m.p. 214-215°.

d) 4-Chloro-4'-Methyl-N-Nitrosobenzanilide

The nitrosoamide (4.3 g.), decomposed in benzene (200 ml.), yielded p-chlorobenzoic acid (2.2 g., 0.90 m/m.), m.p. 238-240°, mixed m.p. 239-241°. Distillation of the solution gave the following fractions: (a) a colourless liquid (10.3 g.), b.p. 80°, (b) a solid (0.97 g.), b.p. 80°/1 mm., and (c) a residue (0.65 g.).

G.L.C. (10% CAR, 10% SIL/100° and 190°) showed that fraction (a) was pure benzene, and that fraction (b) contained only one compound, the I.R. spectrum of which suggested a substituted biphenyl. Recrystallisation from methanol gave colourless plates (0.95 g.), m.p. 47°. [Found: C, 93.1; H, 6.9%. Calc. for $C_{13}H_{12}$: C, 92.8; H, 7.2%]. The literature m.p. [150] for 4-methylbiphenyl was 48°. The N.M.R. spectrum showed absorption at $\tau$ = 7.65 (3 H) and a complex multiplet at $\tau$ = 2.4-3.2 (9 H). This fraction (b) is therefore 4-methylbiphenyl (0.95 g., 0.37 m/m.).

Fraction (c) was chromatographed on alumina. Elution with ether/benzene (1:1) gave 4'-methyl-4-chlorobenzanilide (0.09 g., 0.02 m/m.), m.p. and mixed m.p. 211-212°. The I.R. spectrum confirmed the identification.

e) 3'-Bromo-4-Chloro-N-Nitrosobenzanilide

Decomposition of the nitroso compound (3.5 g.) in benzene (134 ml.) yielded p-chlorobenzoic acid (1.5 g., 0.92 m/m.), m.p. and mixed m.p. 240-242°. Distillation of the mixture gave the following fractions: (a) a colourless liquid (9.7 g.), b.p. 79-80°, (b) a liquid + a solid (1.8 g.), b.p. 90-92°/0.05 mm., and (c) a residue (0.6 g.).

Fraction (a) was shown to be pure benzene by G.L.C. (10% PEGA, 10% SIL/100° and 200°).

Benzene was added to fraction (b) and the insoluble p-chlorobenzoic acid (0.02 g.), m.p. and mixed m.p. 240-241°, removed. G.L.C. of the solution showed that only one compound was present, with retention time equal to that of 3-bromobiphenyl (1.5 g., 0.62 m/m.). The solvent was removed, leaving a pale yellow liquid whose I.R. spectrum was identical with that of authentic 3-bromobiphenyl.

Fraction (c) yielded only intractable gums when chromatographed on alumina.

f) 2'-Bromo-4-Chloro-N-Nitrosobenzanilide

The nitrosobenzanilide (2.02 g.), decomposed in benzene (75 ml.), yielded p-chlorobenzoic acid (0.74 g., 0.77 m/m), m.p. and mixed m.p. 239-241°. Distillation of the mixture gave the following products: (a) a colourless liquid (12.2 g.), b.p. 79-80°, (b) a pale yellow liquid (0.95 g.), b.p. 100-105°/0.1 mm., and (c) a residue (0.45 g.).

By G.L.C. (10% PEGA, 10% SIL/100° and 200°), fraction (a) was shown to be pure benzene, and fraction (b) was shown to contain one compound, 2-bromobiphenyl (0.95 g., 0.68 m/m.). Fraction (b) was further identified by its I.R. spectrum.

Fraction (c) gave no identifiable products on chromatography.

2. 2',4,6'-Trichloro-N-Nitrosobenzanilide

The nitroso compound (0.9 g.) was stirred overnight in benzene (345 ml.) at room temperature, the apparatus being protected from atmospheric moisture by a drying-tube. To ensure completion of the reaction, the mixture was boiled under reflux for 6 hours, and allowed to cool. No precipitate was formed. The bulk of the solvent was removed by distillation, leaving a solid (0.45 g.) which, from the I.R. spectrum, seemed to be a mixture of p-chlorobenzoic acid and anhydride. By fractional crystallisation from benzene these two compounds were isolated: p-chlorobenzoic acid (0.19 g., 0.001 m/m.), m.p. and mixed m.p. 241-243°, and p-chlorobenzoic anhydride (0.23 g., 0.001 m/m.), m.p. and mixed m.p. 191-192°. Distillation of the solution gave the following

fractions: (a) a colourless liquid (11.4 g.), b.p. 80°, (b) a yellow liquid (1.2 g.), b.p. 90°/10 mm., (c) a mixture of a solid and a liquid (0.65 g.), b.p. 105°/0.05 mm., and (d) a residue (6 g.).

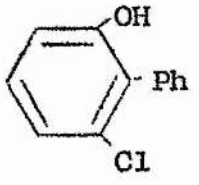
G.L.C. identified fraction (a) as benzene.

The sharp smell and the I.R. spectrum indicated that fraction (b) was possibly p-chlorobenzoyl chloride. A portion (0.5 g.) was added to a suspension of aniline (0.26 g.) in sodium hydroxide solution (10%, 20 ml.). The mixture was shaken and a white solid separated. Recrystallisation of this solid from ethanol gave 4-chlorobenzanilide, identified by m.p. 194°, mixed m.p. 193-194°, and I.R. spectrum. A second portion (0.6 g.) was esterified by boiling under reflux with ethanol (5 ml.) for 4 hours. G.L.C. (10% PEGA, 10% SIL/180°) of the resulting solution showed the products to be 1,2,3-trichlorobenzene (0.075 g.) and ethyl 4-chlorobenzoate (0.48 g.). The original solution must therefore have contained 1,2,3-trichlorobenzene (0.15 g., 0.03 m/m.) and p-chlorobenzoyl chloride (0.92 g., 0.19 m/m.). The solvent was removed from a portion of the esterified solution, and the I.R. spectrum of the product was identical with that of ethyl 4-chlorobenzoate.

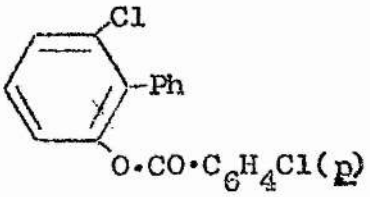
T.L.C. of fraction (c) in benzene showed the presence of 4 components. p-Chlorobenzoic acid was removed by dissolving the other components in benzene. Chromatography on alumina (benzene elution) gave only one solid (0.25 g.), m.p. 64-65°, the I.R. spectrum of which indicated that it contained a hydroxyl group. This compound was later identified as 2-chloro-6-hydroxybiphenyl (See p. 66).

Chromatography of fraction (d) gave the following fractions: (e) a yellow oil (1.87 g.) by elution with light petroleum (b.p. 40-60°)/ benzene (1:1), and (f) 2',4,6'-trichlorobenzanilide (0.9 g., 0.11 m/m.), m.p. and mixed m.p. 193-195°, by elution with benzene/ether (1:1). Further identification of fraction (f) was possible by comparison of the I.R. spectrum with the authentic spectrum.

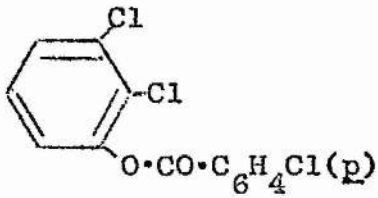
Fraction (e) eventually solidified. T.L.C. showed the presence of only one component, and the I.R. spectrum showed absorption at 1730 $cm.^{-1}$, indicating that it was probably an ester. Recrystallisation from methanol gave colourless needles, m.p. 79-80°. [Found: C, 66.5; H, 3.4; Cl, 20.6%]. The ester (0.48 g.) was hydrolysed[156] by boiling under reflux with sodium hydroxide solution (20%, 10 ml.) for 8 hours. The mixture was made acid to Congo red indicator and then sodium carbonate (5% solution) was added until the solution was alkaline to litmus. On extraction with ether, and evaporation of the solvent, the phenol was obtained. Acidification of the alkaline solution precipitated p-chlorobenzoic acid, m.p. and mixed m.p. 240-242°. The I.R. spectrum of this acid was identical with that from an authentic sample. The phenol (0.19 g.) when recrystallised from light petroleum (b.p. 40-60°), had m.p. 66-67°. [Found: C, 70.2; H, 4.3%]. The N.M.R. spectrum showed a singlet at $\tau$ = 5.2 (hydroxyl), double doublets centred at $\tau$ = 3.12, J = 3, 8.5 c/s. (1 H), at $\tau$ = 2.92, J = 8, 8.5 c/s (1 H) and at $\tau$ = 2.68, J = 3.5, 9 c/s (1 H), and a broad singlet at $\tau$ = 2.53 (5 H). The analysis and N.M.R. spectrum are in accordance with 2-chloro-6-hydroxybiphenyl (14) [$C_{12}H_9ClO$ requires C, 70.4; H, 4.4%].




(14)




(15)




(16)

The original ester would therefore be 2-chloro-6-(p-chlorobenzoyloxy)-biphenyl (15), (1.73 g., 0.19 m/m.). [$C_{19}H_{12}Cl_2O_2$ requires C, 66.5; H, 3.5; Cl, 20.7%]. The above structures are assigned to the unknown compounds by analogy with the ester (16) formed in the reaction of 2',4',6'-trichloro-N-nitrosobenzanilide with carbon tetrachloride (See p. 80 ).

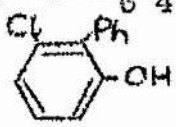
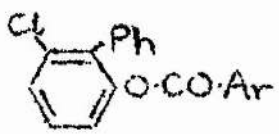
The phenol from fraction (c) and the phenol formed in the hydrolysis of the ester were shown to be identical by I.R. spectra and from the mixed m.p. 65-67°.

3. N-Nitrosoacetanilide [50] (a)

N-Nitrosoacetanilide (3.5 g.) was stirred in benzene (100 ml.) overnight, and then boiled under reflux for 6 hours. The solvent was distilled off at atmospheric pressure, and the residue was distilled (60-65°/0.05 mms.), giving a pale yellow solid. Chromatography on alumina gave biphenyl (1.83 g., 57%), m.p. 69-70, mixed m.p. with authentic sample 69-71°.

TABLE 7

Yields of Products (m/m) Obtained in Reactions of 4-Chloro-N-Nitrosobenzanilides with Benzene

| R in $R.C_6H_4N(NO).CO.Ar$ | H | 4-Me | 4-Br | 3-Br | 2,6-diCl | 2-Br |
|---|---|---|---|---|---|---|
| ArCOOH | 0.33 | 0.90 | 0.80 | 0.92 | 0.05 | 0.77 |
| $(ArCO)_2O$ | 0 | 0 | 0 | 0 | 0.03 | 0 |
| ArCOCl | 0 | 0 | 0 | 0 | 0.19 | 0 |
| PhBr | - | - | 0.003 | - | - | - |
| 1,2,3,-trichloro benzene | - | - | - | - | 0.03 | - |
| $R.C_6H_4.Ph$ | 0.33 | 0.37 | 0.50 | 0.62 | 0 | 0.33 |
| $R.C_6H_4.O.CO.Ar$ | 0.01 | 0 | 0 | 0 | 0 | 0 |
| $Ar.CO.NHC_6H_4R$ | 0 | 0.02 | 0.02 | 0 | 0.11 | 0 |
|  | - | - | - | - | 0.05 | - |
|  | - | - | - | - | 0.19 | - |
| Accountance of Ar | 0.33 | 0.92 | 0.82 | 0.92 | 0.62 | 0.77 |
| Accountance of $R.C_6H_4$- | 0.39 | 0.39 | 0.53 | 0.62 | 0.38 | 0.63 |

(Ar = p.Cl.$C_6H_4$-)

## C Reactions of N-Nitrosoacylarylamines in Carbon Tetrachloride

### I Mono-Substituted 4-Chloro-N-Nitrosobenzanilides

#### (a) General Procedure

The N-nitrosobenzanilide was added to a 200 molar excess of the solvent, and the mixture was stirred overnight at room temperature, the apparatus being protected from atmospheric moisture by a silica-gel guard tube. To ensure completion of the reaction, the mixture was then boiled under reflux for 6 hours, when the solution became very dark in colour. The solution was allowed to cool, and the resultant precipitate was removed. In all cases this proved to be p-chlorobenzoic acid, and was recrystallised from acetic acid. Identification involved comparison of the I.R. spectrum with that from an authentic sample, m.p. and mixed m.p. with the authentic sample. The bulk of the solvent was removed by distillation and, on cooling the solution, a further precipitate was observed. This was found to be p-chlorobenzoic anhydride, and was recrystallised from dry benzene. This compound also was identified by m.p., mixed m.p. and comparison of its I.R. spectrum with that of an authentic sample. The remaining solution was transferred to a small-scale distillation apparatus and all volatile products were removed successively by distillation (a) at atmospheric pressure (b) at 10-15 mm. and (c) at 0.02-0.05 mm. The involatile residue was chromatographed on alumina.

Control experiments showed that neither the acid chloride nor the acid anhydride was hydrolysed to the acid under the reaction conditions.

(b) 4-Chloro-N-Nitrosobenzanilide

4-Chloro-N-nitrosobenzanilide (7.4 g.) was allowed to decompose in carbon tetrachloride (300 ml.). p-Chlorobenzoic acid (1.71 g., 0.45 m/m.), m.p. 239-240°, mixed m.p. 240-241°, and p-chlorobenzoic anhydride (1.05 g., 0.15 m/m.), m.p. 190°, mixed m.p. 190-191° were produced. Distillation of the solution gave the following fractions: (a) a colourless liquid (18.5 g.), b.p. 76.5°, (b) a colourless liquid (1.1 g.), b.p. 131-133°/760 mm., (c) a yellow solid (1.2 g.), b.p. 100°/0.2 mm., and (d) a residue (1.1 g.).

G.L.C. analysis (10% PEGA, 10% SIL/80°) showed that fraction (a) was pure carbon tetrachloride.

The I.R. spectrum of fraction (b) was identical with that of an authentic sample of chlorobenzene. Analysis of fraction (b) by G.L.C. (10% PEGA, 10% SIL/80°) showed the presence of chlorobenzene (0.93 g., 0.25 m/m.).

Recrystallisation of fraction (c) from ethanol gave phenyl 4-chlorobenzoate, m.p. and mixed m.p. 103-104°. The I.R. spectrum of this product was identical with that of the authentic ester. G.L.C. analysis (2% NPGS, 10% SIL/130°) confirmed that fraction (c) was pure phenyl 4-chlorobenzoate (1.00 g., 0.13 m/m.).

Fraction (d), on chromatography on alumina, gave only intractable gums.

A similar reaction, carried out under an atmosphere of nitrogen, gave identical results.

To investigate the possibility of phosgene being one of the products, an aqueous aniline trap was connected to the reaction vessel and a stream of nitrogen was passed through the reaction to carry any gaseous products into the trap. This had been shown to be an effective method for trapping phosgene, [34] but, in this case, no diphenylurea was found in the trap although the yields of other products were identical with those in the previous reactions.

(c) 4' Bromo-4-Chloro-N-Nitrosobenzanilide

The nitroso compound (7.4 g.) was decomposed in carbon tetrachloride (300 ml.). The precipitated p-chlorobenzoic acid (1.65 g., 0.49 m/m.), m.p. and mixed m.p. 240-242°, and p-chlorobenzoic anhydride (1.2 g., 0.19 m/m.), m.p. and mixed m.p. 190-191°, were isolated. Distillation of the remaining solution gave the following fractions: (a) a colourless liquid (3.4 g.), b.p. 76.5°, (b) a pale yellow solid (2.2 g.), b.p. 90-93°/15 mm., (c) a pale yellow liquid (25 m.g.), b.p. 105°/15 mm., (d) an orange solid (0.53 g.), bath temp. 150°/0.1 mm., and (e) a residue (2.1 g.).

Fraction (a) and the main distillate were shown by G.L.C. analysis (10% PEGA, 10% SIL/110°) to contain 1,4-dichlorobenzene (0.32 g., 0.10 m/m.).

G.L.C. analysis (10% PEGA, 10% SIL/110°) showed that fraction (b) contained p-dichlorobenzene (0.47 g., 0.15 m/m.), p-bromochlorobenzene (1.1 g., 0.26 m/m.), and p-dibromobenzene (0.26 g., 0.05 m/m.). These three compounds could not be separated by T.L.C. Preparative G.L.C. gave three colourless solids: (i) p-dichlorobenzene, m.p. and mixed

m.p. 50-51°, (ii) p-bromochlorobenzene, m.p. and mixed m.p. 64-66°, and (iii) p-dibromobenzene, m.p. 84-85°, mixed m.p. 85-86°. The I.R. spectra of these three compounds were identical with those of the authentic samples.

The pungent odour and the I.R. spectrum of fraction (c) suggested that this fraction was p-chlorobenzoyl chloride. Aniline was added, giving an immediate white precipitate, recrystallisation of which from ethanol gave white crystals, m.p. 193-194°, mixed m.p. with authentic 4-chlorobenzanilide 194°. The I.R. spectra of this compound and of 4-chlorobenzanilide were identical. This fraction was thus identified as p-chlorobenzoyl chloride (24 mg., 0.01 m/m.).

Recrystallisation of fraction (d) from methanol gave a compound with m.p. 93-94°, which showed that this was not the expected 4-bromophenyl 4-chlorobenzoate. The I.R. spectrum was identical with that of authentic 4-chlorophenyl 4-chlorobenzoate (lit.[144] m.p. 95°), and mixed m.p. was 93-94°. However, G.L.C. analysis (2% NPGS, 10% SIL/190°) showed the presence of two components, 4-chlorophenyl 4-chlorobenzoate (0.32 g., 0.06 m/m.) and 4-bromophenyl 4-chlorobenzoate (0.05 g., 0.01 m/m.). The two compounds could not be separated by T.L.C., p-Chlorobenzoic acid (0.11 g.) was also isolated from this fraction.

The residue was chromatographed on alumina. Elution with benzene/ether (1:1) gave a brown solid (0.35 g.), which on recrystallisation from benzene/ethanol (1:1) gave yellow needles (0.3 g.), m.p. 181-182°. [Found: C, 44.2; H, 2.5; N, 7.9%]. The I.R. spectrum showed strong absorption at 1700 $cm.^{-1}$. The structure of this compound has not yet been determined.

In an attempt to discover phosgene among the reaction products, a second experiment was carried out, and the carbon tetrachloride distillate was examined. No phosgene was detected with phosgene test-paper, and addition of aniline to the carbon tetrachloride distillate yielded only a trace (3 mg.) of solid, which was shown (m.p. 198° and mixed m.p. 197-8°) to be aniline hydrochloride. However, after a few days, the distillates became brown, and the presence of phosgene was indicated both by smell and by the blue colour produced with phosgene test-paper. Addition of aniline then gave a thick, white, water-soluble precipitate with m.p. 192-3°.. The I.R. spectrum of this compound showed a strong peak at 2020 cm.$^{-1}$ indicating an amine hydrochloride. The brown colour of the solution was discharged by the addition of cyclohexene, but, due to the low concentration, no conclusive detection of 1,2-dibromocyclohexane was possible.

In a similar experiment, the distillate was examined immediately on 4 columns at 50-60°, but no peak corresponding to any possible phosgene precursor could be seen. The distillate was examined at regular intervals, but no further information was obtained.

(d) 4-Chloro-4'-Nitro-N-Nitrosobenzanilide

The nitroso compound (3.23 g.) was allowed to decompose in carbon tetrachloride (390 ml.). When the solution was heated, nitrous fumes were visible in the condenser. p-Chlorobenzoic acid

(2.85 g., 0.68 m/m.), m.p. 240-241°, mixed m.p. 242-243°, and p-chlorobenzoic anhydride (0.72 g., 0.09 m/m.), m.p. 190-192°, mixed m.p. 191-192°, were isolated. Distillation of the solution gave the following fractions: (a) a colourless liquid (16.2 g.), b.p. 76.5°, (b) a yellow solid (1.5 g.), b.p. 116-118°/12 mm., (c) an orange solid (1.1 g.), bath temp. 160°/0.02 mm., and (d) a residue (1.2 g.).

G.L.C. analysis (10% PEGA, 10% SIL/135°) showed that fraction (a) was pure carbon tetrachloride.

The I.R. spectrum of fraction (b) suggested it to be p-chloronitrobenzene. Recrystallisation from methanol gave a compound with m.p. 83° and mixed m.p. with authentic p-chloronitrobenzene 84°. G.L.C. analysis as for fraction (a) showed that fraction (b) contained two components, p-chloronitrobenzene (1.36 g., 0.32 m/m.), and p-dichlorobenzene (0.03 g., 0.02 m/m.). These two compounds could not be separated by T.L.C.

Fraction (c) was recrystallised from methanol, giving 4-chlorophenyl 4-chlorobenzoate (0.80 g., 0.12 m/m.), m.p. and mixed m.p. 94-95°. The I.R. spectrum of this compound was identical with that of the authentic sample. G.L.C. analysis (2% NPGS, 10% SIL/200°) confirmed the presence of only one ester, 4-chlorophenyl 4-chlorobenzoate (0.80 g., 0.11 m/m.). p-Chlorobenzoic acid (0.2 g.) was present in this fraction.

Fraction (d) was chromatographed on alumina, but no identifiable products were obtained.

(e) 4-Chloro-4'-Methyl-N-Nitrosobenzanilide

4-Chloro-4'-methyl-N-nitrosobenzanilide (10 g.) was decomposed in carbon tetrachloride (450 ml.). p-Chlorobenzoic acid (4.5 g., 0.79 m/m.), m.p. 239-240°, mixed m.p. 240-241°, and p-chlorobenzoic anhydride (0.62 g., 0.06 m/m.), m.p. and mixed m.p. 192-193°, were removed. Distillation of the solution gave the following fractions: (a) a colourless liquid (3.3 g.), b.p. 76-77°, (b) a colourless liquid (0.90 g.), b.p. 53-55°/12 mm., (c) an orange solid (0.14 g.) bath temp. 130°/0.05 mm., and (d) a residue (0.3 g.).

Analysis of fraction (a) by G.L.C. (10% PEGA, 10% SIL/100°) identified p-chlorotoluene (0.23 g., 0.04 m/m.).

The I.R. spectrum of fraction (b) was identical to that of authentic p-chlorotoluene. G.L.C. analysis of fraction (b) (10% PEGA, 10% SIL/100°) showed that fraction (b) contained p-chlorotoluene (0.33 g., 0.16 m/m.) with a trace of carbon tetrachloride.

Benzene was added to fraction (c) and the insoluble p-chlorobenzoic acid (0.07 g.) filtered off. The solution was analysed by G.L.C. (2% NPGS, 10% SIL/190°), and p-tolyl 4-chlorobenzoate (0.05 g., 0.005 m/m.) was shown to be present. The ester was separated from the acid by chromatography on alumina (5 g.). The ester was recrystallised from ethanol, giving m.p. and mixed m.p. 98-100°. The identity of this compound was confirmed by comparison of the I.R. spectra. Chromatography of fraction (d)

yielded only intractable gums.

(f) 3'-Bromo-4-Chloro-N-Nitrosobenzanilide

The nitroso compound (9.7 g.), decomposed in carbon tetrachlorid (395 ml.), gave p-chlorobenzoic acid (2.55 g., 0.57 m/m.), m.p. 240-241°, mixed m.p. 241-242°, and p-chlorobenzoic anhydride (1.03 g., 0.13 m/m.), m.p. 189-191°, mixed m.p. 190-192°. Distillation of the reaction mixture then gave the following fractions: (a) a colourless liquid (9.3 g.), b.p. 76-77°, (b) a colourless liquid (2.0 g.), b.p. 69-72°/12 mm., (c) a yellow solid sublimate (0.15 g.), bath temp. 170°/0.02 mm., and (d) a residue (3.0 g.).

Fraction (a) was shown by G.L.C. analysis (10% PEGA, 10% SIL/120°) to contain only carbon tetrachloride.

The I.R. spectrum of fraction (b) was similar to that of m-bromochlorobenzene. This fraction was shown by G.L.C. (10% PEGA, 10% SIL/120°) to contain five components, chlorobenzene (0.004 g., 0.001 m/m.), bromobenzene (0.005 g., 0.001 m/m.), m-dichlorobenzene (0.04 g., 0.01 m/m.), m-dibromobenzene (0.11 g., 0.02 m/m.), and m-bromochlorobenzene (1.76 g., 0.32 m/m.). These compounds could not be separated by T.L.C. The I.R. spectrum of a mixture of these five compounds was identical with that of fraction (b).

Benzene was added to fraction (c), and the insoluble p-chlorobenzoic acid (0.11 g.) removed by filtration. G.L.C. analysis (2% NPGS, 10% SIL/200°) showed that the solution contained 3-bromophenyl 4-chlorobenzoate (0.02 g., 0.002 m/m.). Evaporation of the solvent and recrystallisation of the solid from ethanol.....

gave 3-bromophenyl 4-chlorobenzoate, m.p. 93-95°, mixed m.p. 94-97°.

Chromatography of fraction (d) gave only tars which were not further investigated.

(g) 2'-Bromo-4-Chloro-N-Nitrosobenzanilide

2'-Bromo-4-chloro-N-nitrosobenzanilide (3.9 g.) was decomposed in carbon tetrachloride (140 ml.). The presence of phosgene was indicated by a blue colouration on phosgene test-paper, but no diphenylurea was formed in an aniline trap. p-Chlorobenzoic acid (0.52 g., 0.29 m/m), m.p. and mixed m.p. 241-243°, and p-chlorobenzoic anhydride (0.59 g., 0.17 m/m.), m.p. 189-191°, mixed m.p. 190-191°, were produced. Distillation of the solution gave the following fractions: (a) a pale yellow liquid (14.3 g.), b.p. 76-77°, (b) a yellow liquid (0.98 g.), b.p. 80-85°/15 mm., (c) a yellow solid (0.12 g.), b.p. 90-100°/0.15 mm., and (d) a residue (1.32 g.).

G.L.C. analysis (2% NPGS, 3% APL/90°) showed that fraction (a) was pure carbon tetrachloride.

G.L.C. analysis of fraction (b) [2% NPGS, 3% APL/90°] showed the presence of o-dichlorobenzene (0.20 g., 0.12 m/m.), o-bromochlorobenzene (0.34 g., 0.15 m/m.), and o-dibromobenzene (0.30 g., 0.11m/m). These compounds could not be separated by T.L.C. Proparative G.L.C. (20% APL/200°) gave three colourless liquids, which, by comparison of the I.R. spectra with those of authentic samples, were shown to be o-dichlorobenzene, o-bromochlorobenzene and o-dibromobenzene. This fraction had a pungent smell, and,

on the addition of aniline, 4-chlorobenzanilide (0.01 g.), m.p. 190-192°, mixed m.p. 191-192° was precipitated, i.e. fraction (b) also contained p-chlorobenzoyl chloride (0.007 g., 0.005 m/m.).

Analysis of fraction (c) by G.L.C. (2% NPGS, 3% APL/220°) showed that it contained only one ester, 2-chlorophenyl 4-chlorobenzoate (0.03 g., 0.01 m/m.). This was separated from p-chlorobenzoic acid by chromatography on alumina, followed by recrystallisation from ethanol. The product had m.p. 58-60°, mixed m.p. with authentic 2-chlorophenyl 4-chlorobenzoate 59-60°.

The residue was chromatographed on alumina. Elution with benzene gave a brown oil which, on the addition of ether, gave a yellow solid (0.11 g.). This was recrystallised from benzene, and had m.p. 228-229°. [Found: C, 44.0; H, 2.4; N, 7.9%]. Sodium fusion showed that this solid contained nitrogen and bromine, while the I.R. spectrum showed absorption at 1690 cm.$^{-1}$ (>C=O) and 3390 cm.$^{-1}$ (>N-H). This compound has not yet been identified.

TABLE 8

Yields of Products (m/m) Obtained in Reactions of Monosubstituted 4-Chloro-N-Nitrosobenzanilides with Carbon Tetrachloride.

| R in $R \cdot C_6H_4 \cdot N(NO) \cdot CO \cdot Ar$ | H | p-Br | p-$NO_2$ | p-Me | m-Br | o-Br |
|---|---|---|---|---|---|---|
| ArCOOH | 0.45 | 0.49 | 0.38 | 0.79 | 0.57 | 0.29 |
| $(ArCO)_2O$ | 0.15 | 0.19 | 0.09 | 0.06 | 0.13 | 0.17 |
| $R \cdot C_6H_4 \cdot Cl$ | 0.26 | 0.26 | 0.32 | 0.20 | 0.32 | 0.15 |
| $R \cdot C_6H_4Br$ | - | 0.05 | - | - | 0.02 | 0.11 |
| PhCl | - | - | - | - | 0.001 | - |
| PhBr | - | - | - | - | 0.001 | - |
| $p\text{-}Cl \cdot C_6H_4 \cdot Cl$ | - | 0.25 | 0.02 | - | - | - |
| $m\text{-}Cl \cdot C_6H_4 \cdot Cl$ | - | - | - | - | 0.01 | - |
| $o\text{-}Cl \cdot C_6H_4 \cdot Cl$ | - | - | - | - | - | 0.12 |
| $R \cdot C_6H_4 \cdot O \cdot CO \cdot Ar$ | 0.13 | 0.003 | - | 0.005 | 0.002 | - |
| $p\text{-}Cl \cdot C_6H_4 \cdot O \cdot COAr$ | - | 0.06 | 0.11 | - | - | - |
| $o\text{-}Cl \cdot C_6H_4 \cdot O \cdot COAr$ | - | - | - | - | - | 0.01 |
| $Ar \cdot CO \cdot Cl$ | - | 0.01 | - | - | - | 0.005 |
| Accountance of $R \cdot C_6H_4$ | 0.44 | 0.63 | 0.34 | 0.21 | 0.35 | 0.33 |
| Accountance of Ar- | 0.93 | 0.94 | 0.97 | 0.92 | 0.93 | 0.95 |

$Ar = p \cdot Cl \cdot C_6H_4$

2. o-Disubstituted 4-Chloro-N-Nitrosobenzanilides

a) 2',4,6'-Trichloro-N-Nitrosobenzanilide

The nitroso compound (9.5 g.) was added to carbon tetrachloride (400 ml.) and immediately dissolved. The mixture was stirred at room temperature overnight, the apparatus being protected from atmospheric moisture by a drying-tube. The mixture was then boiled under reflux for 6 hours, nitrous fumes being visible in the condenser. On cooling the solution, a brown solid (0.95 g.) was deposited. All attempts to purify this compound by recrystallisation, sublimation and chromatography have so far failed. On distilling off the bulk of the solvent, a second brown solid (1.42 g.) was obtained. This, too, defied all attempts at purification. Distillation of the solution gave the following fractions: (a) a colourless liquid (8.9 g.), b.p. 76-78°, (b) a yellow liquid (2.27 g.), b.p. 103-5°/10 mm., (c) an orange solid sublimate (0.36 g.), bath temp. 160°/0.15 mm., and (d) a residue (3.45 g.).

Analysis of fraction (a) by G.L.C. (10% PEGA, 10% SIL/100° and 150°) showed only carbon tetrachloride present.

Fraction (b) had a pungent odour and the I.R. spectrum indicated, by comparison with the spectrum of an authentic sample, that it was p-chlorobenzoyl chloride. A portion (0.38 g.) was esterified by boiling under reflux with ethanol (3 ml.) for 5 hours. Analysis of the resulting solution by G.L.C. (10% PEGA, 10% SIL/130°) showed the presence of 1,2,3-trichlorobenzene (0.038 g.) and ethyl 4-chlorobenzoate (0.38 g.). The I.R. spectra of the product after esterification and the authentic ester were identical. A second portion (0.5 g.) was added to a suspension of aniline (0.26 g.) in sodium hydroxide solution (10%, 20 ml.). The mixture was shaken vigorously and a white solid separated. Recrystallisation of this solid from ethanol gave 4-chlorobenzanilide, m.p. 194°, mixed m.p. 193-194°. The I.R. spectrum was identical with that of authentic 4-chlorobenzanilide. Fraction (b) thus contains 1,2,3-trichlorobenzene (0.22 g., 0.05 m/m.) and p-chlorobenzoyl chloride (2.05 g., 0.45 m/m.).

Fraction (c), on recrystallisation from ethanol, gave (i) p-chlorobenzoic anhydride (0.03 g., 0.004 m/m.), m.p. and mixed m.p. 191-192°, (ii) a white solid (0.23 g.) m.p. 117-119°, and (iii) p-chlorobenzoic acid (0.09 g., 0.02 m/m.), m.p. 239-240°, mixed m.p. 239-241°. The I.R. spectrum of fraction c(ii) was identical with that of 2,3-dichlorophenyl 4-chlorobenzoate. Mixed m.p. with the authentic ester was 118-119°. G.L.C. analysis (2% NPGS, 10% SIL/200°) showed the presence of only one compound, 2,3-dichlorophenyl 4-chlorobenzoate (0.21 g., 0.025 m/m.).

Chromatography of fraction (d) gave, by elution with benzene/ether (1:1), 2',4,6'-trichlorobenzanilide (0.74 g., 0.006 m/m.), m.p. and mixed m.p. 190-191°, and I.R. spectrum identical with that of the authentic sample.

Attempts to trap phosgene in this reaction using an aqueous aniline trap failed to produce any diphenylurea, but chloride ions were shown to be present in the trap by means of silver nitrate/nitric acid.

b) 4-Chloro-2',4',6'-Tribromo-N-Nitrosobenzanilide

The nitroso compound (9.95 g.) was dissolved in carbon tetrachloride (280 ml.) and the mixture was stirred overnight as before. After boiling under reflux for 6 hours, the mixture was allowed to cool, but no precipitate was obtained. There was no evidence of nitrous fumes in the reaction vessel.

When the bulk of the solvent had been removed by distillation, a precipitate did form. The I.R. spectrum indicated that this solid was neither p-chlorobenzoic acid nor anhydride, but was probably a mixture of an ester and the starting benzanilide. T.L.C. on alumina showed the presence of two components. The solid was therefore chromatographed on alumina, the following fractions being obtained: (a) light petroleum (b.p. 40-60°)/benzene (1:1) elution yielded a white solid (1.65 g.), m.p. 100°, and (b) benzene/ether (1:1) elution gave 4-chloro-2',4',6'-tribromobenzanilide (1.4 g.), identified by its I.R. spectrum and by the

m.p. 209-211° and mixed m.p. 210-212°. The I.R. spectrum of fraction (a) showed strong absorption at 1740 $cm.^{-1}$, suggesting that this compound might be an ester. The identity of this compound will be discussed later (p. 83).

Distillation of the remaining solution gave the following fractions: (c) a colourless liquid (10.1 g.), b.p. 76.5°, (d) a colourless liquid (0.03g.), b.p. 110°/11 mm., (e) a yellow solid sublimate (0.14 g.), bath temp. 130°/11 mm., (f) an orange solid sublimate (0.3 g.), bath temp. 150°/0.05 mm., and (g) a residue (4.3 g.).

Fraction (c) was shown by G.L.C. (10% PEGA, 10% SIL/130°) to be pure carbon tetrachloride.

From the I.R. spectrum and sharp smell, fraction (d) appeared to be p-chlorobenzoyl chloride. Esterification of this fraction was carried out by boiling it under reflux with ethanol (1 ml.) for 3 hours. The solvent was removed from a portion of the solution, and the I.R. spectrum of the product was shown to be identical with that of authentic ethyl 4-chlorobenzoate. G.L.C. (10% PEGA, 10% SIL/190°) of the solution showed the presence of one component, ethyl 4-chlorobenzoate (0.03 g.), which corresponds to the initial formation of p-chlorobenzoyl chloride (0.03 g., 0.01 m/m.).

Fractions (e) and (f) were combined after T.L.C. had shown that they contained the same two components. Benzene was added, and the insoluble p-chlorobenzoic acid (0.15 g.) removed by filtration. Chromatography of the solution gave a white solid

(0.25 g.), m.p. 90-93°, whose I.R. spectrum was almost identical to that of 1,2,3,5-tetrabromobenzene. However, G.L.C. (2% NPGS, 10% SIL/120°) of this solid showed the presence of two components, 1,2,3,5-tetrabromobenzene (0.19 g., 0.02 m/m.) and 1-chloro-2,4,6-tribromobenzene (0.05 g., 0.007 m/m.). These components could not be separated by T.L.C.

Fraction (g) was chromatographed on alumina after T.L.C. had shown that two compounds were present, the following products being obtained: (h) a white solid (0.3 g.), m.p. 183°, by elution with light petroleum (b.p. 40-60°)/benzene (1:1) and (j) 4-chloro-2',4',6'-tribromobenzanilide (1.0 g.), by elution with benzene/ether (1:1), identified by its I.R. spectrum, its m.p. 210-211° and mixed m.p. 211-212° with the authentic sample.

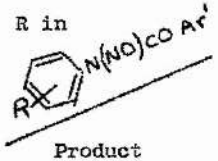
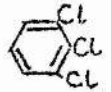
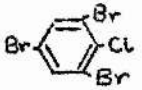
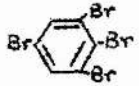
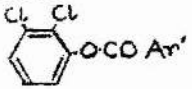
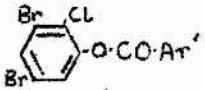
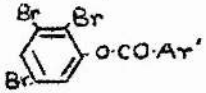
Fractions (a) and (h) had identical I.R. spectra and their mixed m.p. was 183-8°. These two fractions were combined for identification. The I.R. spectrum and the analysis [Found: (i) C, 34.3; H, 1.6%, (ii) C, 35.2; H, 1.6%] supported neither a tribromophenyl 4-chlorobenzoate [Calc. C, 33.3; H, 1.3%] nor a chloro-dibromophenyl 4-chlorobenzaote [Calc. C, 36.7; H, 1.4%]. The ester was hydrolysed in an attempt to identify the phenol and the acid. [cf. Ref. 156]. The ester (0.5 g.) was boiled under reflux with sodium hydroxide (20%, 5 ml.) for 5 hours. Since solid was still present in the reaction mixture, ethanol (2 ml.) was added and the mixture was boiled under reflux for a further

2 hours. The solid (unchanged ester) was removed and the solution made acid to Congo Red indicator with sulphuric acid (2 N), when the acid separated as a faint precipitate. Sodium carbonate (5% solution) was added until the solution was alkaline to litmus and the precipitated acid dissolved. The phenol was extracted into ether, giving, on evaporation of the solvent, a yellow solid. Recrystallisation from light petroleum (b.p. 60-80°) gave a white solid (0.20 g.), m.p. 82-83°. Acidification of the solution precipitated p-chlorobenzoic acid (0.07 g.), identified by m.p. and mixed m.p. 239-241° and by its I.R. spectrum. The N.M.R. spectrum of the phenol showed absorption at $\tau$ = 4.3 (hydroxyl) and doublets, centred at $\tau$ = 2.59 (1 H) and $\tau$ = 2.31 (1 H), J = 2.1 c/s, consistent with a 2,3,5-trisubstituted phenol. This spectrum was very similar to those of 2,3,5-tribromophenol and 2-chloro-3,5-dibromophenol. The I.R. spectrum was very similar to that of 2,3,5-tribromophenol. G.L.C. (2% NPGS/170°) showed that the phenolic portion contained two components, 2-chloro-3,5-dibromophenol and 2,3,5-tribromophenol in the ratio 1:6·2. The original ester fraction must therefore have been a mixture of 2-chloro-3,5-dibromophenyl 4-chlorobenzoate (0.31 g., 0.04 m/m.), and 2,3,5-tribromophenyl 4-chlorobenzoate (1.93 g., 0.21 m/m.). A mixture of authentic samples of these two esters was prepared and the I.R. spectrum was found to be identical with that of fractions (a) and (h). This was further support for the identity of the two compounds, which could not be separated.

TABLE 9

Yields of Products (m/m)[a] Obtained in Reactions of o-Disubstituted 4-Chloro-N-Nitrosobenzanilides with Carbon Tetrachloride

$Ar' = p\text{-}Cl\text{-}C_6H_4 -$

| R in  Product | 2',6'-Dichloro | 2',4',6'-Tribromo |
|---|---|---|
| Ar'COOH | 0.02 | 0.02 |
| $(Ar'CO)_2O$ | 0.005 | 0 |
| Ar'COCl | 0.45 | 0.01 |
|  | 0.04 | - |
|  | - | 0.00? |
|  | - | 0.02 |
| Anilide | 0.02 | 0.26 |
|  | 0.03 | - |
|  | - | 0.04 |
|  | - | 0.21 |
| Accountance of Ar' | 0.59 | 0.55 |
| Accountance of R-  | 0.15 | 0.54 |

3. Substituted 4-Bromo-N-Nitrosobenzanilides [$R \cdot C_6H_4N(NO) \cdot CO \cdot C_6H_4 \cdot Br(p)$]

(a) 4-Bromo-4'-Nitro-N-Nitrosobenzanilide

The nitroso compound (6.83 g.) was stirred in carbon tetrachloride (277 ml.) overnight, the apparatus being protected from atmospheric moisture by a silica-gel guard tube. The mixture was then refluxed for 6 hours to complete the reaction, nitrous fumes being evolved. The precipitate obtained on cooling the reaction mixture, and also that obtained by removing the bulk of the solvent, were shown by I.R. spectra to be a mixture of p-bromobenzoic acid and anhydride. To effect a separation, they were extracted with sodium hydroxide solution (2N, 50 ml.) to remove the acid. The solid left was recrystallised from benzene, giving p-bromobenzoic anhydride (1.00 g., 0.13 m/m.), m.p. 216-217°, mixed m.p. 216-218°. The I.R. spectra of this compound and of the authentic anhydride were identical. The alkaline solution was acidified (HCl, 2N) giving p-bromobenzoic acid (2.56 g., 0.65 m/m.), m.p. 249-250°, mixed m.p. 249-251°.

Distillation of the solution gave the following fractions: (a) a colourless liquid (15.6 g.), b.p. 75-76.5°, (b) a solid (1.2 g.), b.p. 110°/13 mm., (c) a solid (0.16 g.), b.p. 60°/0.1 mm., (d) a solid sublimate (0.62 g.), bath temp. 170°/0.1 mm. and (e) a residue (1.1 g.).

Analysis of fraction (a) by G.L.C. (10% PEGA, 10% SIL/130°) showed that it was pure carbon tetrachloride.

The I.R. spectra of fractions (b) and (c) were almost identical with that of authentic p-chloronitrobenzene. A sample of fraction (b), after recrystallisation from ethanol, had m.p. 83-85°, mixed m.p. with authentic p-chloronitrobenzene 84-86°. G.L.C. (10% PEGA, 10% SIL/130°) showed that fractions (b) and (c) contained the same four components, and analysis of the combined fractions showed p-bromonitrobenzene (0.03 g., 0.01 m/m.), p-chloronitrobenzene (1.16 g., 0.40 m/m.), p-dichlorobenzene (0.07 g., 0.02 m/m.), and p-bromochlorobenzene (0.007 g., 0.02 m/m.). The compounds could not be separated other than by G.L.C.

By G.L.C. (10% SIL, 2% NPGS/200°), fraction (d) was shown to contain only 4-chlorophenyl 4-bromobenzoate (0.44 g., 0.07 m/m). Chromatography on alumina, followed by recrystallisation from methanol gave 4-chlorophenyl 4-bromobenzoate, m.p. 100-101°, mixed m.p. 101-102°. The I.R. spectrum was identical with that of the authentic ester.

Fraction (e) was chromatographed on alumina, but only intractable tars were obtained.

(b) 4,4'-Dibromo-N-Nitrosobenzanilide

4,4'-Dibromo-N-nitrosobenzanilide (9.57 g.) and carbon tetrachloride (355 ml.) were reacted as in the previous experiment. p-Bromobenzoic acid (2.3 g., 0.46 m/m.) m.p. 248-250°, mixed m.p. 249-250°, and p-bromobenzoic anhydride (1.6 g., 0.17 m/m.), m.p. and mixed m.p. 217-218° were isolated. Distillation gave the

following fractions: (a) a colourless liquid (12.3 g.), b.p. 75-80°, (b) a yellow solid (2.24 g.), b.p. 75-80°/12 mm., (c) a liquid (0.16 g.), b.p. 42-45°/0.1 mm., (d) a solid sublimate (0.41 g.), bath temp. 180°/0.1 mm., and (e) a residue (1.5 g.).

G.L.C. of fraction (a) (10% PEGA, 10% SIL/150°) showed the presence of traces of p-dichlorobenzene (0.06 g., 0.01 m/m.) and p-bromochlorobenzene (0.05 g., 0.01 m/m.) in the carbon tetrachloride.

The I.R. spectrum of fraction (b) was indicative of p-bromochlorobenzene; a sample, after recrystallisation from methanol, had m.p. 63°, mixed m.p. with authentic p-bromochlorobenzene 63-65°. However, G.L.C. (10% PEGA, 10% SIL/130°) showed that this fraction contained three components, p-dichlorobenzene (0.50 g., 0.14 m/m.), p-bromochlorobenzene (1.53 g., 0.32 m/m.), and p-dibromobenzene (0.39 g., 0.07 m/m.). A mixture of authentic samples of these three compounds had an I.R. spectrum identical with that obtained from fraction (b). These three components could not be separated by T.L.C.

Fraction (c) was a solid when stored in ice, but liquified on warming to room temperature. This behaviour, the I.R. spectrum and the sharp smell suggested that this fraction might be p-bromobenzoyl chloride. A sample (0.05 g.) was added to a suspension of aniline (0.02 g.) in sodium hydroxide solution (2N, 5 ml.). The white precipitate was recrystallised from methanol, giving 4-bromobenzanilide, identified by comparison of I.R. spectrum with

that of an authentic sample, by m.p. and mixed m.p. 198-200°. A second sample (0.1 g.) was esterified by boiling under reflux with ethanol (2 ml.) for 2 hours. The presence of ethyl 4-bromobenzoate (0.1 g.) was shown by G.L.C. (10% SIL, 10% PEGA/195°) and also by the I.R. spectrum of the product obtained after evaporation of the solvent from a portion of the solution. Fraction (c) was therefore p-bromobenzoyl chloride (0.15 g., 0.03 m/m.).

Fraction (d) was stirred in benzene and the insoluble p-bromobenzoic acid (0.14 g.) filtered off. The solution was chromatographed on alumina and the product was recrystallised from ethanol to give white needles (0.25 g.) m.p. 98-99°, mixed m.p. with authentic 4-chlorophenyl 4-bromobenzoate 99-100°. The I.R. spectrum was identical with that of the authentic ester. However, G.L.C. (10% SIL, 2% NPGS/190°) showed the presence of both 4-chlorophenyl 4-bromobenzoate (0.2 g., 0.03 m/m.) and 4-bromophenyl 4-bromobenzoate (0.04 g., 0.005 m/m.). These could not otherwise be separated.

Chromatography of fraction (e) produced a yellow solid by elution with light petroleum (b.p. 40-60°)/benzene (1:1). Recrystallisation of this solid from benzene/ethanol gave yellow needles (0.25 g.), m.p.179-180°. From the I.R. spectra and the mixed m.p. (180-181°) this compound appears to be identical with the unidentified compound from the reaction of 4'-bromo-4-chloro-N-nitrosobenzanilide with carbon tetrachloride (p. 71).

TABLE 10

Yields of Products (m/m) Obtained in Reactions of Substituted 4-Bromo-N-Nitrosobenzanilides with Carbon Tetrachloride

Ar = p.Br.$C_6H_4$ -

| R in $R.C_6H_4.N(NO).CO.Ar$ / Product | p-$NO_2$ | p-Br |
|---|---|---|
| ArCOOH | 0.65 | 0.46 |
| $(ArCO)_2O$ | 0.13 | 0.17 |
| $R.C_6H_4Br$ | 0.01 | 0.07 |
| $R.C_6H_4Cl$ | 0.40 | 0.33 |
| p-Br.$C_6H_4Cl$ | 0.002 | - |
| p-Cl.$C_6H_4Cl$ | 0.02 | 0.15 |
| p-Cl.$C_6H_4O.COAr$ | 0.07 | 0.03 |
| ArCOCl | - | 0.03 |
| $R.C_6H_4O.COAr$ | - | 0.005 |
| Accountance of Ar | 0.93 | 0.87 |
| Accountance of $R.C_6H_4$- | 0.50 | 0.49 |

4. N-Nitrosoacetanilide (c.f. Ref. 34)

a) N-Nitrosoacetanilide (3.2 g.) was dissolved in carbon tetrachloride (135 ml.). Almost immediately a solid was precipitated. The mixture was stirred overnight at room temperature and then boiled under reflux for 6 hours, when the solid decomposed. Phosgene was detected by phosgene test-paper. The solvent was removed by distillation. The residue was shown by G.L.C.analysis (2% NPGS, 10% SIL/80°), to contain chlorobenzene (0.77 g., 0.35 m/m.) and phenyl acetate (0.13 g., 0.05 m/m.). Chromatography of the solution on alumina by elution with light petroleum (b.p. 40-60°) gave a colourless liquid, which was shown by G.L.C. to be a mixture of chlorobenzene and phenyl acetate. Distillation of this mixture gave (a) a colourless liquid (0.59 g.), b.p. 128-130°, with I.R.spectrum identical with that of authentic chlorobenzene, and (b) a colourless liquid (0.09 g.), bath temp. 120°/0.1 mm., with I.R. spectrum identical with that of phenyl acetate. No other products were obtained.

b) Estimation of Acetic Acid and Acetic Anhydride in Carbon Tetrachloride Solution.

Since acid anhydrides had been isolated in the previous reactions in carbon tetrachloride, it was possible that acetic anhydride might be formed in the reaction of N-nitrosoacetanilide in carbon tetrachloride. It was therefore necessary to establish a method for the estimation of acetic anhydride in the presence of acetic acid in carbon tetrachloride solution.

(i) A solution of acetic acid (0.636 g.) and acetic anhydride (0.201 g.) in carbon tetrachloride (135 ml.) was extracted with sodium hydroxide solution. Back titration with standard acid, using bromothymol blue as indicator, gave a value of 0.920 g. for the total acid present in the solution. Acetic acid produced by hydrolysis of the acetic anhydride would amount to 0.240 g., making the total acetic acid present in the solution equal to 0.926 g. Extraction with alkali obviously gives an accurate determination of the total acetic acid originally present together with the acetic acid produced by hydrolysis of acetic anhydride.

(ii) To a solution of acetic acid (0.634 g.) and acetic anhydride (0.203 g.) in carbon tetrachloride (135 ml.) was added aniline (0.4 g.). The mixture was shaken vigorously and allowed to stand for half an hour. The reaction mixture was extracted with alkali. Back titration as described in (i) above gave a value of 0.750 g. for the total acid present. However, in this case, only 1 mole of acid is formed from the anhydride by reaction with aniline, and so the expected value for the total acid in the solution would be 0.753 g. acetic acid.

It is therefore possible to estimate accurately the amounts of both acetic acid and acetic anhydride in a solution by finding (a) total acetic acid from acetic acid + acetic anhydride and (b) total acid content after reacting the anhydride with aniline. The difference (a) - (b) is equivalent to one half of the acetic acid produced by hydrolysis of the acetic anhydride.

The total anhydride concentration can be easily calculated, and hence the amount of acid from (a).

(iii) Decomposition of N-Nitrosoacetanilide in Carbon Tetrachloride

N-Nitrosoacetanilide (2.4 g.) was allowed to decompose in carbon tetrachloride (100ml.) as described in section (a). A portion of the solution was extracted with sodium hydroxide solution. Back titration gave the total quantity of acetic acid in the mixture as 0.76 g. To another portion of the reaction mixture was added aniline. Back titration then gave a value of 0.61 g. for the total acetic acid in the solution. The difference in these values can be accounted for by the presence of acetic anhydride (0.22 g., 0.15 m/m.), which would give the amount of acetic acid present originally as 0.43 g. (0.54 m/m.).

Attempts to distil the acetic anhydride from the reaction mixture failed.

(b). N-Nitrosoacetanilide (3.9 g.) was allowed to decompose in carbon tetrachloride (100 ml.) as above. The solvent was removed and the remaining solution was distilled, giving the following liquid fractions: (a) 9.3 g., b.p. 77°; (b) 4.1g., b.p.78-85°; (c) 0.85 g., b.p. 85-125°; (d) 0.39 g., b.p. 125-140°; (e) 0.19 g., b.p. 110°/12 mm., and (f) a residue (0.75 g.).

Fraction (a) gave a white solid (0.100 g.) on addition of aniline. The I.R. spectrum of this solid showed absorption at 2020 $cm.^{-1}$, indicating an amine hydrochloride.

The m.p. was 194°, mixed m.p. with authentic aniline hydrochloride 195-196°.

Addition of aniline to fraction (b) gave a solid (0.04 g.). The I.R. spectrum of this solid showed the presence of aniline hydrochloride, but also a compound with >N-H and >C=O, possibly acetanilide. The mother liquor deposited crystals of acetanilide (0.02 g.), identified by its I.R. spectrum, m.p. and mixed m.p. The I.R. spectrum of fraction (b) showed absorption at 1840 $cm.^{-1}$ and 1770 $cm.^{-1}$ which corresponded to the absorption in the acetic anhydride spectrum, and also absorption at 1720 $cm.^{-1}$ which could be due to acetic acid.

The I.R. spectrum of fraction (c) showed absorption at 1810 $cm.^{-1}$, which is correct for acetyl chloride. This fraction fumed on exposure to air. These fumes were acidic.

Addition of aniline to fraction (c) produced a white solid (0.07 g.) whose I.R. spectrum was identical with that of the solid obtained by the addition of aniline to fraction (b).

Fraction (d) reacted in a similar way to fraction (c), giving a white solid (0.02 g.).

Fraction (e) was shown by G.L.C. and its I.R. spectrum to be phenyl acetate.

No phosgene was detected until the distillates had been standing for a few days. The presence of phosgene was then shown by the blue colouration produced with phosgene test-paper.

The residue, fraction (f), was unaffected by acid hydrolysis, by alkaline hydrolysis and by reduction with zinc and hydrochloric acid. Sodium fusion showed the presence of nitrogen and chlorine. No identifiable products were obtained when this fraction was chromatographed.

## IV. REACTIONS OF N-NITROSOACYLARYLAMINES IN THE PRESENCE OF ARYNE-TRAPPING REAGENTS

### A Reactions in Carbon Tetrachloride

#### 1. Furan as Trapping Agent

##### (a) 4-Chloro-N-Nitrosobenzanilide

The nitroso compound (7.62 g., 0.029 mole) and furan (1.98 g., 0.029 mole) were stirred at room temperature in carbon tetrachloride (400 ml.) overnight. The mixture was boiled under reflux for 6 hours, and allowed to cool. p-Chlorobenzoic acid (3 g., 0.65 m/m), m.p. and mixed m.p. 239-241° and p-chlorobenzoic anhydride (0.79 g., 0.09 m/m) m.p. and mixed m.p. 190-191°, were isolated as in the reaction without a benzyne trap. G.L.C. of the solution (10% PEGA, 10% SIL/145°) showed that there was no 1,4-dihydronaphthalene-1,4-endoxide (the benzyne/furan adduct) present. The solution was distilled as before and chlorobenzene (0.95 g., 0.23 m/m) and phenyl 4-chlorobenzoate (0.28 g., 0.04 m/m) isolated. No 1,4-dihydronaphthalene-1,4-endoxide was obtained on distillation.

The nitroso compound was then allowed to decompose in carbon tetrachloride in the presence of a 20 molar excess of furan. Again no adduct was found.

Control experiments showed that the adduct was stable under the reaction conditions.

No phenylfuran was detected in either of the reactions.

b) 4-Chloro-4'-Methyl-N-Nitrosobenzanilide

The nitroso compound (5.0g.) with a 10-molar excess of furan (12.45 g.) was allowed to decompose in carbon tetrachloride (270 ml.) as in (a) above. p-Chlorobenzoic acid (2.06 g., 0.72 m/m.) and p-chlorobenzoic anhydride (0.31 g., 0.06 m/m.) were isolated. G.L.C. of the solution showed no volatile products with retention time comparable with either the aryne/furan adduct (6-methyl-1,4-dihydronaphthalene-1,4-endoxide) or 2-p-tolyl furan. Distillation of the solution yielded p-chlorotoluene (0.58 g., 0.05 m/m.), identified by its I.R. spectrum and G.L.C. as before (p. 74 ), but no aryne/furan adduct was isolated. [lit.[165] b.p. 57°/0.2 mm.].

(2) Anthracene as Trapping Agent

(a) 4-Chloro-N-Nitrosobenzanilide

The nitroso compound (5.7 g.) and anthracene (7.7 g.) were stirred in carbon tetrachloride (200 ml.) overnight at room temperature, the contents of the reaction vessel being protected from atmospheric moisture by a drying tube. The mixture was boiled under reflux for 6 hours, and allowed to cool. The precipitate (6.47 g.)

was shown by T.L.C. to contain no triptycene, and the I.R. spectrum showed peaks corresponding to p-chlorobenzoic acid and to anthracene, but none corresponding to p-chlorobenzoic anhydride. The acid was extracted into sodium hydroxide (2N, 150 ml.). On acidification, p-chlorobenzoic acid (2.03 g., 0.61 m/m.), m.p. and mixed m.p. 241-243°, was precipitated.

The solvent was removed by distillation, giving a further precipitate (2.2 g.), the I.R. spectrum of which indicated that it contained p-chlorobenzoic anhydride but no acid. The anhydride was removed by boiling the mixture under reflux with sodium hydroxide (2N, 100 ml.). After filtering off the residual solid, the alkaline layer was acidified, giving p-chlorobenzoic acid (1.02 g.) which was equivalent to the original formation of p-chlorobenzoic anhydride (0.93 g., 0.15 m/m.).

The anthracene in these two precipitates was removed by dissolving the solids in hot xylene (100 ml.), adding maleic anhydride (5 g.) and boiling under reflux for 30 minutes. After allowing the mixture to stand for 3½ hours, sodium hydroxide solution (2N, 100 ml.) was added and the mixture was again boiled under reflux for 2 hours. The alkaline layer was removed, ether (100 ml.) was added and the organic layer was washed with water (3 x 50 ml.). Removal of the solvent gave traces of brown tars, which showed no triptycene on T.L.C.

The reaction mixture was distilled, giving chlorobenzene (0.50 g., 0.25 m/m.), which was identified by its I.R. spectrum and by

G.L.C., as previously described (p.69). Anthracene was removed from the residue in the flask by boiling it under reflux with maleic anhydride (2 g.) in xylene (100 ml.) as above. The solid remaining after evaporation of the xylene was examined by T.L.C., and showed a fluorescent spot with the same $R_f$ value as authentic triptycene. Chromatography on alumina and elution with light petroleum (b.p. 40-60°) gave a yellow solid (0.33 g.), which on recrystallisation from benzene gave triptycene (0.29 g., 0.05 m/m.)., m.p. 257-8°, mixed m.p. 258-259°. The I.R. and N.M.R. spectra of this compound were identical with those of the authentic sample, the N.M.R. spectrum showing absorption at $\tau$ = 4.6(2 H) and a complex multiplet at $\tau$ = 2.5-3.1(12 H).

(b) N-Nitrosoacetanilide

N-Nitrosoacetanilide (7.5 g.) and anthracene (3 g.) were reacted in carbon tetrachloride (150 ml.) as above. The solid was removed and the solvent was distilled off, leaving a dark-coloured solid. The anthracene was removed from these precipitates by boiling under reflux with maleic anhydride in xylene, as above. No triptycene was detected in the residue. The solution was chromatographed on alumina, but again no triptycene was isolated.

3. 2,3,4,5-Tetraphenylcyclopentadienone as Trapping Agent

(a) N-Nitrosoacetanilide

N-Nitrosoacetanilide (3.2 g.) and 2,3,4,5-tetraphenyl-cyclopentadienone (15.2 g.) were allowed to react in carbon tetrachloride

(135 ml.). The reaction mixture was stirred overnight at room temperature, and then boiled under reflux for 8 hours. The dark solid was filtered off, and T.L.C. showed that it contained no 1,2,3,4-tetraphenylnaphthalene. After removal of the bulk of the solvent by distillation, G.L.C. of the residue showed the presence of chlorobenzene (<0.01 m/m.). T.L.C. of the residue showed the presence of a compound with the same $R_f$ value as authentic 1,2,3,4-tetraphenylnaphthalene.

Chromatography of the residue gave the following products: (a) a white solid (1.92 g.) by elution with light petroleum (b.p. 40-60°)/benzene (9:1), (b) a dark red solid, 2,3,4,5-tetraphenylcyclopentadienone, (67%) by elution with benzene, and (c) a brown tar (3.2 g.) by elution with methanol.

Recrystallisation of fraction (a) from acetic acid gave 1,2,3,4-tetraphenylnaphthalene (1.38 g., 0.21 m/m.), m.p. 198-199°, mixed m.p. 199-200°. The I.R., U.V., and N.M.R. spectra were identical with those of the authentic sample. Fraction (c) had a phenolic smell. Attempts to purify it failed, and it was not further investigated.

(b) m-Substituted and Unsubstituted N-Nitrosobenzanilides

(i) General Method

The nitroso compound, together with a 1 molar excess of 2,3,4,5-tetraphenylcyclopentadienone, was stirred in carbon tetrachloride overnight at room temperature, the reaction being kept free

from moisture. After being boiled under reflux for 6 hours to complete the reaction, the mixture was allowed to cool. The appropriate benzoic acid was precipitated, and was identified by its I.R. spectrum, m.p. and mixed m.p. after recrystallisation. The bulk of the solvent was removed by distillation, and the resultant dark precipitate in no case showed anhydride carbonyl absorption in the I.R. spectrum. A portion of the solution was retained for analysis by G.L.C. The remaining solution [which was shown by T.L.C. to contain the appropriate tetraphenylnaphthalene] together with the dark solid precipitate, was adsorbed on to alumina and chromatographed to yield the tetraphenylnaphthalene(s). The precipitated carboxylic acids were separated from any 2,3,4,5-tetraphenylcyclopentadienone by extraction into alkali and subsequent acidification of the alkaline layer.

(ii) 4-Chloro-N-Nitrosobenzanilide

4-Chloro-N-Nitrosobenzanilide (6.8 g.) was allowed to decompose in carbon tetrachloride (350 ml.) in the presence of 2,3,4,5-tetraphenylcyclopentadienone (20.6 g.) giving p-chlorobenzoic acid (2.0 g., 0.49 m/m), m.p. and mixed m.p. 242-244°. There was no trace of p-chlorobenzoic anhydride.

G.L.C. analysis (10% PEGA, 10% SIL/85°) of a portion of the solution showed the presence of chlorobenzene equivalent to total yield of 0.1 g. (0.04 m/m).

Chromatography of the residue gave the following fractions: (a) a white solid (3.65 g.) by elution with light petroleum (b.p. 40-60°)/benzene (9:1), (b) 2,3,4,5-tetraphenylcyclopentadienone (70%) by elution with light petroleum (b.p. 40-60°)/benzene (1:1) and (c) a brown gum (1.0 g.) by elution with methanol. Recrystallisation of fraction (a) from acetic acid gave 1,2,3,4-tetraphenylnaphthalene (3.5 g., 0.32 m/m), m.p. 197-199°, mixed m.p. 198-199°. The I.R., U.V., and N.M.R. spectra were identical to those of the authentic sample. Fraction (c) was not further investigated.

(iii) 4-Chloro-N-Nitrosobenzanilide in the Presence of Water

A similar reaction, using 4-chloro-N-nitrosobenzanilide from the same batch as that in experiment (ii) above, was carried out in the presence of water.

4-Chloro-N-nitrosobenzanilide (2.55 g.), 2,3,4,5-tetraphenyl-cyclopentadienone (7.3 g.) and water (0.2 g., 1 molar proportion) were reacted in carbon tetrachloride (136 ml.). p-Chlorobenzoic acid (1.08 g., 0.69 m/m.), m.p. and mixed m.p. 240-242°, and p-chlorobenzoic anhydride (0.35 g., 0.14 m/m.), m.p. and mixed m.p. 189-191°, were isolated as described in the reaction without 2,3,4,5-tetraphenylcyclopentadienone (p. 69). G.L.C. (2% NPGS, 10% SIL/85°) showed that no chlorobenzene was present.

Chromatography of the solution gave the following fractions: (a) a yellow solid (0.15 g.) by elution with light petroleum (b.p. 40-60°)/benzene (9:1), (b) 2,3,4,5-tetraphenylcyclopentadienone, by

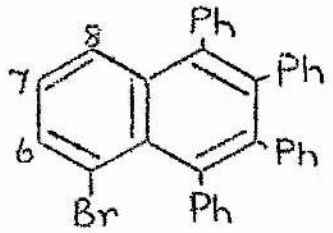
elution with benzene, and (c) a brown gum by elution with methanol. Recrystallisation of fraction (a) from acetic acid gave 1,2,3,4-tetraphenylnaphthalene (0.10 g., 0.02 m/m), m.p. and mixed m.p. 198-200°. The I.R., N.M.R. and U.V. spectra were identical with those of the authentic sample.

(iv) 3'-Bromo-4-Chloro-N-Nitrosobenzanilide

The nitrosobenzanilide (7.5 g.) and 2,3,4,5-tetraphenylcyclopentadienone (16.7 g.) were allowed to react in carbon tetrachloride (218 ml.). There was a vigorous evolution of nitrogen almost immediately, p-Chlorobenzoic acid (2.8 g., 0.82 m/m), m.p. 239-241°, mixed m.p. 240-241° was removed. m-Bromochlorobenzene (0.10 g., 0.02 m/m) and only a trace of 3-bromophenyl 4-chlorobenzoate were identified by G.L.C. (10% SIL, 2% NPGS/110° and 180° respectively).

Chromatography of the mixture gave the following products: (a) a colourless liquid (0.06 g.) by elution with light petroleum (b.p. 40-60°), (b) a white solid (8.0 g.) by elution with light petroleum (b.p. 40-60°)/benzene (5:1), (c) 2,3,4,5-tetraphenylcyclopentadienone (20%) by elution with light petroleum (b.p. 40-60°)/benzene (1:1), (d) a brown gum (0.3 g.) by elution with ether and (e) a brown gum (1.1 g.) by elution with methanol.

Recyrstallisation of fraction (b) from acetic acid gave white plates (7.9 g.) m.p. 235-236°. [Found: C, 79.5; H, 4.7%. $C_{34}H_{23}Br$ requires C, 79.8; H, 4.5%]. The U.V. and I.R. spectra suggested that it was a substituted tetraphenylnaphthalene. The N.M.R. spectrum was consistent with 5-bromo-1,2,3,4-tetraphenylnaphthalene (17) and details are given overleaf.




(17)

| Absorption (τ) | Nature of Absorption | J (c/s) | Proton(s) responsible for absorption |
|---|---|---|---|
| 3.21 | broad singlet (10 H) | - | phenyl |
| 2.91 | broad singlet (5 H) | - | phenyl |
| 2.81 | broad singlet (5 H) | - | phenyl |
| 2.89 | double doublet (1 H) | 8.7, 7.0 | $H_{(7)}$ |
| 2.35 | double doublet (1 H) | 8.7, 1.7 | probably $H_{(6)}$ |
| 2.20 | double doublet (1 H) | 7.0, 1.4 | probably $H_{(8)}$ |

The three phenyl absorptions are due to the substitutent being in the 5-position. By comparison with the N.M.R. spectrum from 6-bromo-1,2,3,4-tetraphenylnaphthalene (see p. 56 ) it was possible to establish that the compound isolated in this experiment was pure 5-bromo-1,2,3,4-tetraphenylnaphthalene, and that it contained no 6-bromo-1,2,3,4-tetraphenylnaphthalene. The total yield was 7.9 g. (0.70 m/m).

The I.R. spectrum of fraction (a) was identical with that of m-bromochlorobenzene. Fractions (c) and (d) were not further investigated.

(v) 4-Chloro-3'-Methyl-N-Nitrosobenzanilide

The nitroso compound (6.5 g.) was allowed to decompose in carbon tetrachloride (240 ml.) in the presence of 2,3,4,5-tetraphenylcyclopentadienone (18 g.), giving p-chlorobenzoic acid (2.6 g., 0.71 m/m), m.p. and mixed m.p. 240-241°. G.L.C. of the solution (10% PEGA, 10% SIL/100°) showed the presence of m-chlorotoluene (0.15 g., 0.05 m/m). Chromatography of the residue gave the following fractions: (a) a colourless liquid (0.10 g.) by elution with light petroleum (b.p. 40-60°), (b) a white solid (3.65 g.) by elution with light petroleum (b.p. 40-60°)/benzene (4:1), (c) 2,3,4,5-tetraphenylcyclopentadienone (60%) by elution with light petroleum (b.p. 40-60°)/benzene (1:1), (d) a brown tar (0.3 g.) by elution with ether, and (e) a brown tar (0.62 g.) by elution with methanol.

The I.R. spectrum of fraction (a) was identical with that of m-chlorotoluene.

Recyrstallisation of fraction (b) from acetic acid gave white plates (3.5 g.), m.p. 221-224°. [Found: C, 94.1; H, 6.0%. Calc. for $C_{35}H_{26}$; C, 94.1; H, 5.9%]. The U.V. and I.R. spectra were indicative of a substituted 1,2,3,4-tetraphenylnaphthalene. The N.M.R. spectrum showed singlets at $\tau$ = 8.03 and $\tau$ = 7.61 attributed to methyl protons in two different environments, and also five phenyl absorptions at $\tau$ = 3.20, 3.18, 2.86, 2.84 and 2.79. These absorptions are almost identical with those found in the N.M.R. spectra of 5-methyl-1,2,3,4-tetraphenylnaphthalene ($\tau$ = 8.02, 3.18, 2.85 2.79)

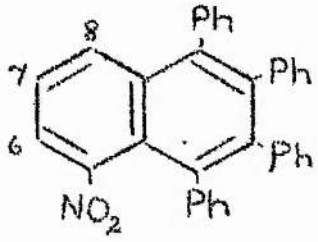
and 6-methyl-1,2,3,4-tetraphenylnaphthalene (τ = 7.6, 3.2, 2.33) [see p. 56]. The N.M.R. spectrum of a mixture of authentic 5-methyl- and 6-methyl-1,2,3,4-tetraphenylnaphthalene showed absorptions at τ = 8.02, and 7.61, attributed to the methyl protons and phenyl absorptions at τ = 3.20, 3.17, 2.87, 2.83, 2.79. From the analysis and the N.M.R. spectrum, it can therefore be concluded that this fraction is a mixture of 5-methyl-1,2,3,4-tetraphenylnaphthalene and 6-methyl-1,2,3,4-tetraphenylnaphthalene. From the integrals in the N.M.R. spectrum, the ratio of these two compounds was found to be 5-methyl: 6-methyl = 7:4; i.e. 5-methyl-1,2,3,4-tetraphenylnaphthalene (2.24 g., 0.21 m/m) and 6-methyl-1,2,3,4-tetraphenylnaphthalene (1.28 g., 0.12 m/m).

Fractions (d) and (e) were not further investigated.

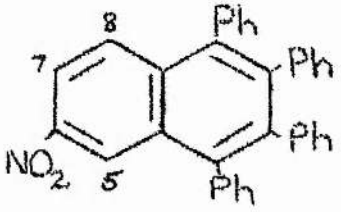
(vi) 4-Chloro-3'-Nitro-N-Nitrosobenzanilide

The nitroso compound (8.6 g.), 2,3,4,5-tetraphenylcyclopentadienone (21 g.) and carbon tetrachloride (400 ml.) were stirred at room temperature. Nitrogen evolution began almost immediately. Nitrous fumes were visible when the mixture was heated. p-Chlorobenzoic acid (3.72 g., 0.84 m/m), m.p. 240-242°, mixed m.p. 241-242° was removed. G.L.C. of the solution showed that no m-chloronitrobenzene was present. Chromatography of the residue gave the following products: (a) 2,3,4,5-tetraphenylcyclopentadienone (25%) by elution with light petroleum (b.p. 40-60°)/benzene (4:1), (b) a yellow solid (8.3 g.) by elution with light petroleum (b.p. 40-60°)/benzene (1:1) and (c) a brown solid (0.65 g.) by elution with ether/methanol (9:1).

Recrystallisation of fraction (b) from acetic acid gave yellow needles (3.1 g.), m.p. 254°. [Found: C, 85.2; H, 5.2; N, 3.0%]. This compound darkened on exposure to light. The N.M.R. spectrum was consistent with the structure 5-nitro-1,2,3,4-tetraphenylnaphthalene (18) and not 6-nitro-1,2,3,4-tetraphenylnaphthalene (19).




(18)




(19)

The N.M.R. spectrum showed three broad singlets at $\tau$ = 3.13 (10 H), 2.9 (5 H) and 2.79 (5 H), attributed to phenyl absorption, and double doublets, centres $\tau$ = 2.68 ($H_7$) [J = 3.2, 7.2 c/s], $\tau$ = 2.3 (probably $H_6$) [J = 7.3, 1.9 c/s] and $\tau$ = 2.13 (probably $H_8$) [J = 8.3, 2.0 c/s]. The three phenyl resonances are due to the presence of the substituent in the 5-position. The only other possible isomer (19) would be expected to show only 2 phenyl resonances [c.f. 6-methyl 1,2,3,4-tetraphenylnaphthalene (p.56) and 6-bromo-1,2,3,4-tetraphenylnaphthalene (p.56)] and a doublet with J = 9c/s for $H_8$, a double doublet with J=9 and 2c/s for $H_7$ and a doublet with J=2c/s for $H_5$. The I.R. spectrum, the analysis and the N.M.R. spectrum therefore indicate that this compound is 5-nitro-1,2,3,4-tetraphenylnaphthalene (8.1 g., 0.63 m/m). [$C_{34}H_{23}NO_2$ requires C, 85.5; H, 4.9; N, 2.9%].

Fraction (c) was recrystallised from ethanol giving 4-chloro-3'-nitrobenzanilide (0.45 g., 0.05 m/m), m.p. and mixed m.p. 186-188°. The I.R. spectra of this and the authentic sample were identical.

(vii) 4-Nitro-N-Nitrosobenzanilide

Decomposition of the nitroso compound (6.54 g.) and 2,3,4,5-tetraphenylcyclopentadienone (13.6 g.) in carbon tetrachloride (250 ml.) gave p-nitrobenzoic acid (1.9 g., 0.44 m/m), m.p. and mixed m.p. 237-239°, (Lit.[150] 241-5°) after recrystallisation from ethanol. G.L.C. (10% SIL, 10% PEGA/90°) of a portion of the solution showed the presence of chlorobenzene (0.45 g. total, 0.16 m/m). Phenyl 4-nitrobenzoate (0.61 g. total, 0.10 m/m) was also shown to be present by G.L.C. (2% NPGS, 2% CAR/190°).

Chromatography of the residue gave the following fractions: (a) a colourless liquid (0.38 g.) by elution with light petroleum (b.p. 40-60°), (b) a yellow solid (0.5 g.) by elution with light petroleum (b.p. 40-60°)/benzene (9:1) (c) a white solid (1.5 g.) by elution with light petroleum (b.p. 40-60°)/benzene (4:1), (d) 2,3,4,5-tetraphenylcyclopentadienone (33%) by elution with light petroleum (b.p. 40-60°)/benzene (1:1), (e) a brown gum (0.69 g.) by elution with ether and (f) a brown gum (1.1 g.) by elution with methanol.

The I.R. spectrum of fraction (a) was identical with that of chlorobenzene.

Recrystallisation of fraction (b) from ethanol gave pale yellow needles m.p. 128-130°, mixed m.p. 128-130° with authentic phenyl 4-nitrobenzoate. The I.R. spectrum of this compound was identical with that of the authentic sample.

Recrystallisation of fraction (c) gave 1,2,3,4-tetraphenylnaphthalene (1.35 g., 0.14 m/m), m.p. 200°, mixed m.p. 200-201°. I.R., U.V., and N.M.R. spectra were identical with the authentic spectra.

Fractions (e) and (f) were intractable tars.

(viii) 4-Methyl-N-Nitrosobenzanilide

The nitroso compound (2.3 g.) was reacted with carbon tetrachloride (196 ml.) in the presence of 2,3,4,5-tetraphenylcyclopentadienone (17.4 g.), yielding p-toluic acid (0.67 g., 0.52 m/m), m.p. and mixed m.p. 180-182°. G.L.C. (10% PEGA, 10% SIL/80°) of a portion of the solution showed the absence of chlorobenzene, but indicated the presence of phenyl 4-methylbenzoate (0.2 g., total, 0.10 m/m) [10% SIL, 2% NPGS/150°].

The remaining solution was chromatographed, giving the following fractions: (a) a white solid (0.15 g.) by elution with light petroleum (b.p. 40-60°), (b) a white solid (1.3 g.) by elution with light petroleum (b.p. 40-60°)/benzene (4:1), (c) 2,3,4,5-tetraphenylcyclopentadienone (71%) by elution with light petroleum (b.p. 40-60°)/benzene (1:1), (d) a brown gum (0.32 g.) by elution with benzene/ether (1:1) and (e) a brown gum (0.16 g.) by elution with methanol.

Recrystallisation of fraction (a) from ethanol gave phenyl 4-methylbenzoate, m.p. and mixed m.p. 73-75°. The I.R. spectra of this compound and the authentic ester were identical.

Recrystallisation of fraction (b) from acetic acid gave 1,2,3,4-tetraphenylnaphthalene (1.2 g., 0.29 m/m), m.p. and mixed m.p. 201-202°. Identification was also possible by comparing the I.R., U.V., and N.M.R. spectra with those of the authentic sample.

Fractions (d) and (e) were not investigated further.

C o- and p- Substituted 4-Chloro-N-Nitrosobenzanilides

(i) General Method

The nitroso compound was allowed to decompose in carbon tetrachloride in the presence of 2,3,4,5-tetraphenylcyclopentadienone. The mixture was stirred overnight at room temperature and then boiled under reflux for 6 hours to complete the reaction. The precipitate obtained on cooling the mixture, and also that left after removal of the bulk of the solvent, showed the same I.R. spectra, mixtures of p-chlorobenzoic acid, p-chlorobenzoic anhydride and 2,3,4,5-tetraphenylcyclopentadienone. No adduct was detected in these precipitates by T.L.C. To separate the components of this mixture, the solid was stirred with sodium hydroxide solution. P-Chlorobenzoic acid was precipitated on acidification of the alkaline solution, and was identified by m.p., mixed m.p. and I.R. spectrum. The residual solid was then boiled under reflux with sodium hydroxide solution to hydrolyse the anhydride. Acidification of the alkaline solution gave p-chlorobenzoic acid, from which the yield of p-chlorobenzoic anhydride was calculated. A portion of the reaction

mixture was kept for G.L.C. The remaining solution was chromatographed on alumina.

(ii) 2'-Bromo-4-Chloro-N-Nitrosobenzanilide

The nitroso compound (3.9 g.) was decomposed in carbon tetrachloride (140 ml.) in the presence of 2,3,4,5-tetraphenylcyclopentadienone (8.6 g.). p-Chlorobenzoic acid (0.4 g., 0.24 m/m), m.p. and mixed m.p. 240-242°, and p-chlorobenzoic anhydride (0.74 g., 0.22 m/m), were produced. By G.L.C. (2% NPGS, 3% APL/90°) of a portion of the solution the presence of o-dichlorobenzene (0.01 g. total, 0.01 m/m), o-bromochlorobenzene (0.20 g. total, 0.09 m/m) and o-dibromobenzene (0.34 g. total, 0.13 m/m) was detected. Chromatography of the remaining solution gave the following fractions: (a) a yellow oil (0.36 g.) by elution with light petroleum (b.p. 40-60°), (b) 2,3,4,5-tetraphenylcyclopentadienone by elution with light petroleum (b.p. 40-60°)/benzene (1:1), and (c) a brown tar (0.55 g.) by elution with ether and methanol.

Fraction (a) was the mixture of o-dihalogeno benzenes detected by G.L.C. The I.R. spectrum was identical with that from a mixture of the authentic samples.

Fraction (c) had a phenolic smell. Extraction with alkali and acidification of the alkaline solution failed to yield a product. The acidified solution was then extracted with ether, but no phenol was obtained on evaporation of the solvent.

No 5-bromo-1,2,3,4-tetraphenylnaphthalene was detected.

(iii) 4'-Bromo-4-Chloro-N-Nitrosobenzanilide

The nitroso compound (6.15 g.) was decomposed in carbon tetrachloride (180 ml.) in the presence of 2,3,4,5-tetraphenylcyclopentadienone (13.7 g.). p-Chlorobenzoic acid (0.51 g., 0.18 m/m), m.p. and mixed m.p. 239-241°, and p-chlorobenzoic anhydride (1.28 g., 0.23 m/m) were produced. G.L.C. of a portion of the reaction mixture (10% CAR, 10% SIL/130°) showed the presence of p-dichlorobenzene (0.03 g. total, 0.01 m/m), p-bromochlorobenzene (0.31 g. total, 0.09 m/m), and p-dibromobenzene (0.36 g. total, 0.09 m/m). Only a minute quantity of ester (4-chlorophenyl 4-chlorobenzoate) could be detected by G.L.C.

The mixture was then chromatographed on alumina, giving the following fractions: (a) a white solid (0.70 g.) by elution with light petroleum (b.p. 40-60°), (b) a white solid (0.41 g.) by elution with light petroleum (b.p. 40-60°)/benzene (4:1), (c) 2,3,4,5-tetraphenylcyclopentadienone (75%) by elution with light petroleum (b.p. 40-60°)/benzene (1:1), (d) a brown tar (1.6 g.) by elution with ether, and (e) a brown tar (2.4 g.) by elution with ether/methanol (1:1).

Fraction (a) was identified as the mixture of dihalogeno benzenes detected by G.L.C. The I.R. spectrum was identical with that from a mixture of the authentic compounds.

Recrystallisation of fraction (b) from acetic acid gave 6-bromo-1,2,3,4-tetraphenylnaphthalene (0.38 g., 0.04 m/m),

m.p. and mixed m.p. 243°. The I.R., U.V., and N.M.R. spectra were identical with those of the authentic sample.

Attempts to purify the fractions (d) and (e) resulted in a dark brown solid (3.5 g.) of m.p. 70-120°. The I.R. spectrum of this compound was poorly resolved, but showed a peak at 1750 $cm^{-1}$. This solid is still unidentified.

(iv) 4-Chloro-4'-Methyl-N-Nitrosobenzanilide

The nitroso compound (1.96 g.) was allowed to decompose in carbon tetrachloride (105 ml.) in the presence of 2,3,4,5-tetraphenylcyclopentadienone (5.5 g.). p-Chlorobenzoic acid (0.70 g., 0.63 m/m). m.p. 240-241°, mixed m.p. 240-242° and p-chlorobenzoic anhydride (0.22 g., 0.11 m/m) were produced. The presence of p-chlorotoluene (0.21 g. total, 0.23 m/m) was shown by G.L.C. (10% SIL, 10% CAR/80°) of a portion of the solution. Chromatography of the remaining solution gave the following fractions: (a) a colourless liquid (0.15 g.) by elution with light petroleum (b.p. 40-60°), (b) a white solid (35 mg.) by elution with light petroleum (b.p. 40-60°)/benzene (4:1), (c) 2,3,4,5-tetraphenyl-cyclopentadienone (70%) by elution with light petroleum (b.p. 40-60°)/ benzene (1:1) and (d) a brown gum (1.3 g.) by elution with ether and methanol.

The I.R. spectrum of fraction (a) was identical with that of p-chlorotoluene. Recrystallisation of fraction (b) from acetic acid gave 6-methyl-1,2,3,4-tetraphenylnaphthalene (30 mg., 0.01 m/m).

m.p. 221°, mixed m.p. 222°. The I.R., U.V., and N.M.R. spectra were identical with those of the authentic sample. Fraction (d) was intractable tar and was not further investigated.

(v) 4-Chloro-4'-Nitro-N-Nitrosobenzanilide

The nitrosobenzanilide (8.2 g.), 2,3,4,5-tetraphenylcyclopentadienone (20.5 g.) and carbon tetrachloride (395 ml.) were reacted as described above. Brown fumes appeared when the mixture was heated. p-Chlorobenzoic acid (0.18 g., 0.04 m/m), m.p. and mixed m.p. 239-241°, and p-chlorobenzoic anhydride (1.38 g., 0.18 m/m) were produced. G.L.C. analysis of a portion of the solution (2% NPGS, 10% SIL/115°) detected p-chloronitrobenzene (0.40 g. total, 0.09 m/m), while analysis at 190° showed the presence of 4-chlorophenyl 4-chlorobenzoate (0.45 g. total, 0.09 m/m).

Chromatography of the remaining reaction mixture gave the following compounds: (a) a white solid (0.34 g.) by elution with light petroleum (b.p. 40-60°), (b) a white solid (0.42 g.) by elution with light petroleum (b.p. 40-60°)/benzene (5:1), (c) 2,3,4,5-tetraphenylcyclopentadienone (60%) by elution with light petroleum (b.p. 40-60°)/benzene (1:1), (d) a dark brown solid and tar (3.85 g.) by elution with benzene/ether (1:1), and (e) a dark brown solid (0.42 g.) by elution with methanol.

Fraction (a) was recrystallised from light petroleum (b.p. 60-80°) and was found to be p-chloronitrobenzene, m.p. and mixed m.p. 84-85°. Identification was also possible by comparison of the I.R. spectrum with that of the authentic sample.

Recrystallisation of fraction (b) from ethanol gave 4-chlorophenyl 4-chlorobenzoate, m.p. and mixed m.p. 93-94°. The I.R. spectrum of this and of the authentic ester were identical.

Fraction (e), after recrystallisation from ethanol, gave 4-chloro-4'-nitrobenzanilide (0.33 g., 0.06 m/m), identified by its I.R. spectrum, m.p. and mixed m.p. 221-222°.

Fraction (c) gave a brown solid after being washed with methanol. After chromatography and recrystallisation from ethanol, yellow needles (2.25 g.), m.p. 167-168° [Found: C, 86.0; H, 4.9%. Mol. Wt. 400] were isolated. The I.R. spectrum was very similar to that of 2,3,4,5-tetraphenylcyclopentadienone, showing strong absorption at 1720 $cm^{-1}$. The N.M.R. spectrum showed a complex multiplet at $\tau$ = 2.79-3.4. No nitrogen or halogen was found in this compound. Since the frequency of the carbonyl absorption resembled that of an ester, attempts were made to hydrolyse a portion of the compound (0.18 g.) by boiling under reflux with alkali as already described (p. 83). However, no phenol or acid was isolated, but, instead, a white solid insoluble in alkali was obtained. Chromatography of this solid gave two compounds: (i) 60 mg. and (ii) 40 mg. Both compounds showed absorption at approximately 1660 $cm^{-1}$ in the I.R. spectrum. Fraction (ii) was recrystallised from acetic acid, giving a solid of m.p. 133-136° [Found: C, 87.4; H, 6.1%]. The N.M.R. spectrum of this fraction showed a complex multiplet at $\tau$ = 2-3, with a small singlet at 6.04$\tau$. Attempts to recrystallise fraction (i) were not

very successful. Recrystallisation from acetic acid gave a solid which melted over a wide range (90-100°). These compounds have not yet been identified.

TABLE 11

Yields of Product (m/m) Obtained in Reactions of N-Nitrosobenzanilides with Carbon Tetrachloride in the Presence of 2,3,4,5-Tetraphenylcyclopentadienone

$X \cdot C_6H_4 \cdot N(NO) \cdot CO \cdot C_6H_4 \cdot Y$ (2)

| | X = H | 2'Br | 3'-Br | 4'-Br | 3'-Me | 4'-Me | 3'-$NO_2$ | 4'-$NO_2$ | H | H |
|---|---|---|---|---|---|---|---|---|---|---|
| | Y = Cl | Cl | Cl | Cl | Cl | Cl | Cl | Cl | $NO_2$ | Me |
| Product (Ar = p-Y·$C_6H_4$·) | | | | | | | | | | |
| ArCOOH | 0.49 | 0.24 | 0.82 | 0.18 | 0.71 | 0.63 | 0.84 | 0.04 | 0.44 | 0.52 |
| $(ArCO)_2O$ | 0 | 0.22 | 0 | 0.23 | 0 | 0.11 | 0 | 0.13 | 0 | 0 |
| Adduct | 0.32 | 0 | 0.70 | 0.04 | 0.33 | 0.01 | 0.83 | 0 | 0.14 | 0.29 |
| $X \cdot C_6H_4 \cdot NH \cdot COAr$ | 0 | 0 | 0 | 0 | 0 | 0 | 0.05 | 0.06 | 0 | 0 |
| $X \cdot C_6H_4Cl$ | 0.04 | 0.09 | 0.02 | 0.09 | 0.05 | 0.23 | 0 | 0.09 | 0.15 | 0 |
| $X \cdot C_6H_4Br$ | - | 0.13 | 0 | 0.09 | - | - | - | - | - | - |
| o-Cl·$C_6H_4Cl$ | - | 0.11 | - | - | - | - | - | - | - | - |
| p-Cl·$C_6H_4Cl$ | - | - | - | 0.01 | - | 0 | - | 0 | - | - |
| Ph·O·CO·Ar | 0 | - | - | - | - | - | - | - | 0.10 | 0.10 |
| Ar·O·CO·Ar | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.09 | 0 | 0 |
| Accountance of $X \cdot C_6H_4$ | 0.36 | 0.33 | 0.72 | 0.23 | 0.38 | 0.24 | 0.84 | 0.24 | 0.40 | 0.38 |
| Accountance of Ar | 0.49 | 0.68 | 0.82 | 0.64 | 0.71 | 0.85 | 0.68 | 0.40 | 0.54 | 0.62 |

4. The Relative Efficiencies of Anthracene and Tetraphenylcyclopentadienone as Trapping Agents

Anthracene and 2,3,4,5-tetraphenylcyclopentadienone were allowed to compete for authentic benzyne produced by the reaction of amyl nitrite with anthranilic acid, as described in the preparation of the authentic adducts (p.54 ). When the reaction mixture was chromatographed, tetraphenylnaphthalene (65%) was isolated, but no triptycene could be detected, i.e. Tetraphenylcyclopentadienone is superior to anthracene as a trap for authentic benzyne.

B Reactions of N-Nitrosobenzanilides in Benzene in the presence of 2,3,4,5-Tetraphenylcyclopentadienone

1) 4-Chloro-N-Nitrosobenzanilide

The nitroso compound (3.6 g.), 2,3,4,5-tetraphenylcyclopentadienone (11.1 g.) and benzene (178 ml.) were stirred together overnight at room temperature, the apparatus being protected from atmospheric moisture by a silica-gel guard tube. To ensure complete reaction, the mixture was boiled under reflux for 6 hours, and then allowed to cool. The bulk of the solvent was removed by distillation, leaving a dark solid, the I.R. spectrum of which showed carbonyl absorption corresponding to p-chlorobenzoic acid and 2,3,4,5-tetraphenylcyclopentadienone, but none corresponding to p-chlorobenzoic anhydride. The acid was extracted into alkali and precipitated from the alkaline solution by acidification, giving p-chlorobenzoic acid (1.70 g., 0.79 m/m), m.p. and mixed m.p. 241-243°. The presence of biphenyl (0.09 g., 0.04 m/m) and phenyl 4-chlorobenzoate (0.19 g.,

0.06 m/m) in the reaction mixture was shown by G.L.C. (2% NPGS, 10% SIL/170°).

Chromatography of the reaction mixture gave the following fractions: (a) a white solid (0.09 g.) by elution with light petroleum (b.p. 40-60°), (b) a white solid (0.15 g.) by elution with light petroleum (b.p. 40-60°)/benzene (9:1), (c) a yellow solid (2.3 g.) by elution with light petroleum (b.p. 40-60°)/benzene (4:1), (d) 2,3,4,5-tetraphenylcyclopentadienone (65%) by elution with light petroleum (b.p. 40-60°)/benzene (1:1) and (e) a brown gum (1.5 g.) by elution with ether and methanol.

Fraction (a) was recrystallised from light petroleum (b.p. 60-80°), and was identified as biphenyl by m.p. and mixed m.p. 70-71° and by its I.R. spectrum.

Recrystallisation of fraction (b) from methanol gave phenyl 4-chlorobenzoate, m.p. and mixed m.p. 103-104°. The I.R. spectrum of this compound was identical with the authentic spectrum.

Fraction (c), on recrystallisation from acetic acid, gave 1,2,3,4-tetraphenylnaphthalene (2.2 g., 0.37 m/m), m.p. 199°, mixed m.p. 200°. The I.R., U.V., and N.M.R. spectra were identical with the authentic spectra.

Fraction (e) was not further investigated.

ii) 2'-Bromo-4-Chloro-N-Nitrosobenzanilide

The nitrosoamide (4.0 g.) was allowed to decompose in benzene (145 ml.) in the presence of 2,3,4,5-tetraphenylcyclopentadienone (8.6 g.) as in the previous experiment. p-Chlorobenzoic acid (1.1 g., 0.69 m/m), m.p. and mixed m.p. 240-242° was produced. G.L.C. examination (2% NPGS, 3% APL/160°) showed the presence of 2-bromobiphenyl (0.59 g., 0.21 m/m) in the reaction mixture, together with traces (≪ 0.01 m/m) of biphenyl and bromobenzene.

Chromatography of the reaction mixture gave the following fractions: (a) a liquid (0.50 g.) by elution with light petroleum (b.p. 40-60°)/benzene (4:1), (b) 2,3,4,5-tetraphenylcyclopentadienone by elution with light petroleum (b.p. 40-60°)/benzene (3:1), (c) a brown oil by elution with benzene and (d) a brown gum (1.58 g.) by elution with ether and methanol.

Fraction (a) was identified as 2-bromobiphenyl by comparison of the I.R. spectrum with that of the authentic sample. Fractions (c) and (d) were not further investigated.

No 5-bromo-1,2,3,4-tetraphenylnaphthalene was isolated, and none could be detected by T.L.C.

iii) 3'-Bromo-4-Chloro-N-Nitrosobenzanilide

The nitroso compound (3.5 g.), 2,3,4,5-tetraphenylcyclopentadienone (7.6 g.) and benzene (134 ml.) were stirred together overnight at room temperature, and then boiled under reflux for 6 hours.

The precipitated p-chlorobenzoic acid (1.40 g., 0.8% m/m), m.p. 240-243°, mixed m.p. 241-243° was removed. The presence in the reaction mixture of 3-bromobiphenyl (0.025 g., 0.01 m/m) was shown by G.L.C. (2% NPGS, 10% SIL/150°).

Chromatography of the mixture gave the following fractions: (a) a white solid (3.95 g.) by elution with light petroleum (b.p. 40-60°)/benzene (4:1), (b) 2,3,4,5-tetraphenylcyclopentadienone (25%) by elution with light petroleum (b.p. 40-60°)/benzene (1:1), and (c) brown tars (0.7 g.) by elution with ether and methanol.

Recrystallisation of fraction (a) gave 5-bromo-1,2,3,4-tetraphenylnaphthalene (3.85 g., 0.73 m/m), m.p. 234-235°, mixed m.p. with the previous sample of this adduct 234-235°. I.R., U.V., and N.M.R. spectra were identical with those of the adduct obtained in a similar reaction in carbon tetrachloride. The N.M.R. spectrum showed no absorptions corresponding to 6-bromo-1,2,3,4-tetraphenylnaphthalene.

Fraction (c) was not further investigated.

TABLE 12

Yields of Products (m/m) Obtained in Reactions of Substituted 4-Chloro-N-Nitrosobenzanilides [$X \cdot C_6H_4 \cdot N(NO) \cdot C_6H_4Cl(p)$] With Benzene in the Presence of 2,3,4,5-Tetraphenylcyclopentadienone

| X / Product (Ar=p-Cl·$C_6H_4$-) | H | 2'-Br | 3'-Br |
|---|---|---|---|
| ArCOOH | 0.79 | 0.69 | 0.87 |
| $X \cdot C_6H_4 \cdot C_6H_5$ | 0.04 | 0.21 | 0.01 |
| Ph·O·CO·Ar | 0.06 | - | - |
| Adduct | 0.37 | 0 | 0.73 |
| Accountance of Ar | 0.85 | 0.69 | 0.87 |
| Accountance of $X \cdot C_6H_4$- | 0.47 | 0.21 | 0.74 |

## V. REACTIONS OF N-NITROSOACYLARYLAMINES AT ROOM TEMPERATURE

### A N-Nitrosoacetanilide in Carbon Tetrachloride

When N-nitrosoacetanilide was added to carbon tetrachloride at room temperature, it dissolved immediately, but in a few minutes a precipitate appeared. This precipitate was water soluble, and showed absorption in the I.R. spectrum at 2300 $cm^{-1}$ corresponding to the $-\overset{+}{N}\equiv N$ absorption [159]. When β-naphthol in alkaline solution was added to an aqueous solution of this solid, a red solid, m.p. 133°, was formed. (lit. m.p. for benzeneazo-β-naphthol is 132°). The solid from the reaction mixture is obviously a benzenediazonium salt. An aqueous solution, on treatment with nitric acid and silver nitrate, gave a white precipitate, which survived on heating.. Silver acetate would be soluble under such conditions, and the precipitate must therefore be silver chloride. Benzenediazonium chloride is thus produced as an intermediate in the reaction of N-nitrosoacetanilide with carbon tetrachloride.

### B 3'-Bromo-4-Chloro-N-Nitrosobenzanilide in Carbon Tetrachloride

Under the conditions described above, this reaction also gave a precipitate, which showed similar infra red absorption at 2300 $cm^{-1}$. In this case, however, the salt was mixed with p-chlorobenzoic acid. The mixture was added to water and the insoluble p-chlorobenzoic acid removed. A red dye (m.p. 170-172°) [lit. [153] m.p. for p-bromobenzeneazo-β-naphthol 172-173°] was produced when alkaline β-naphthol was added to the aqueous solution. Treatment

of the aqueous solution with silver nitrate and nitric acid as before again resulted in a white precipitate, which indicated the presence of chloride ions. p-Bromobenzenediazonium chloride is therefore produced as an intermediate in the reaction of p-bromo-N-nitroso-acetanilide with carbon tetrachloride.

C 3'-Bromo-4-Chloro-N-Nitrosobenzanilide in Benzene

In this case, the precipitate was pure p-chlorobenzoic acid, identified by its I.R. spectrum, m.p. and mixed m.p. 239-241°. No diazonium salt was isolated.

## VI. MEASUREMENT OF NITROGEN EVOLUTION IN THE DECOMPOSITION OF N-NITROSOACETANILIDE IN ORGANIC SOLVENTS.

### A N-Nitrosoacetanilide in Carbon Tetrachloride

N-nitrosoacetanilide (0.23 g.) was added to carbon tetrachloride (21 ml.) in a thermostatic bath at 27°. The nitrogen evolution, measured in a nitrometer, corresponded to 45% of the theoretical volume. The benzenediazonium chloride (0.09 g.) produced was suspended in fresh solvent and allowed to decompose at 45°. The nitrogen which was then evolved gave a total nitrogen evolution of 80%.

### B N-Nitrosoacetanilide in Benzene

N-Nitrosoacetanilide (0.1 g.) was added to benzene (3.5 ml.) in a thermostatic bath at 27°. A total nitrogen evolution of 68% was observed. No further nitrogen evolution occurred on increasing the temperature of the bath to 45°.

## VII E.S.R. SPECTRA

The following investigations were carried out in collaboration with Dr. C. Thomson.

### A N-Nitrosoacetanilide in Benzene

Nitrosoacetanilide (0.1 g.) in benzene (0.75 ml.) gave the spectrum attributed by Richardt[75] to the radical Ph - N = N - O·.

### B 4-Chloro-N-Nitrosoacetanilide in Benzene

The nitroso compound (0.09 g.) in benzene (0.75 ml.) gave a spectrum which was atrributed to the radical p-Cl.$C_6H_4$·N=N·O· .

### C N-Nitrosoacetanilide in Carbon Tetrachloride

N-Nitrosoacetanilide (0.09 g.) in carbon tetrachloride (0.65 ml.) gave very small peaks, which were definitely not those of the spectrum produced in (A). This spectrum consisted of 3 very broad bands, widely spaced.

### D 4-Chloro-N-Nitrosobenzanilides in Benzene

4-Chloro-N-Nitrosobenzanilide and 2',4,6'-trichloro-N-nitrosobenzanilide in benzene gave no resolvable signals, even when the reaction mixtures were cooled to -20°C. initially.

Page No.

# DISCUSSION

## REACTIONS OF N-NITROSOBENZANILIDES IN AROMATIC SOLVENTS



## DECOMPOSITION OF N-NITROSOACYLARYLAMINES IN BENZENE AND IN CARBON TETRACHLORIDE IN THE PRESENCE OF DIENES AS ARYNES TRAPS



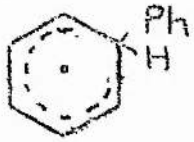
## CONCLUSION

The mechanism of the decomposition of N-nitrosoacetanilide in organic solvents is one of the outstanding problems in organic chemistry. Work carried out prior to this investigation has already been described in the Introduction (p. 6 ) and the various anomalous reactions of N-nitrosoacetanilide as a radical source have been noted there. Reaction schemes, discussed fully in the Introduction (p.15 ), have been advanced to explain the reaction of N-nitrosoacetanilide with benzene, based on the E.S.R. spectrum of an intermediate free radical. Rüchardt *et al.*[25] attribute this spectrum to the phenyl diazotate radical, $Ph\cdot N_2O\cdot$, and their scheme is shown below:

$$Ph\cdot N(NO)\cdot Ac \longrightarrow Ph\cdot N{:}N\cdot OAc \rightleftharpoons Ph\cdot N_2^{+} + AcO^{-}$$

$$Ph\cdot N{:}N\cdot OAc + AcO^{-} \longrightarrow Ph\cdot N_2O^{-} + Ac_2O$$

$$Ph\cdot N_2O^{-} + PhN_2^{+} \longrightarrow Ph\cdot N_2\cdot O\cdot N_2\cdot Ph \longrightarrow Ph\cdot + N_2 + Ph\cdot N_2O\cdot$$

$$Ph\cdot + PhH \longrightarrow \text{  } \xrightarrow{Ph\cdot N_2O\cdot} Ph\cdot Ph + Ph\cdot N_2\cdot CH$$

$$AcO^{-} + Ph\cdot N_2\cdot OH \longrightarrow AcOH + Ph\cdot N_2O^{-}$$

A modification of this scheme, proposed recently by Suschitzky,[160] is shown below:

$$Ph\cdot N(NO)\cdot Ac \rightleftharpoons [Ph\cdot N_2O^{-}\ Ac^{+}] \longrightarrow Ph\cdot N{:}N\cdot O\cdot Ac \rightleftharpoons [PhN_2^{+}\ \bar{O}Ac]$$

$$Ac^{+} + \bar{O}Ac \longrightarrow Ac_2O$$

$$Ph\cdot N_2O^{-} + Ph\cdot N_2^{+} \longrightarrow Ph\cdot N_2\cdot O\cdot N_2\cdot Ph$$

The diazoanhydride then reacts as in Rüchardt's scheme. Acetic acid is produced according to the following sequence of reactions:

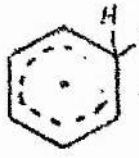
$$Ph{\cdot}N_2OH \longrightarrow Ph{\cdot}N_2^{+}\ \bar{O}H \xrightarrow{Ac^{+}} AcOH + PhN_2^{+}$$

Perkins et al.[77,78] however, claim that the E.S.R. spectrum is due to the intermediate radical [20].

Their proposed scheme is as follows:

$$Ph{\cdot}N{:}N{\cdot}O{\cdot}Ac \longrightarrow Ph\cdot + N_2 + \cdot OAc$$

$$Ph\cdot + Ph{\cdot}N(NO){\cdot}Ac \longrightarrow \begin{array}{l} Ph{\cdot}N{\cdot}O\cdot \\ \quad | \\ Ph{\cdot}N{\cdot}Ac \end{array} \qquad (20)$$

$$Ph\cdot + PhH \longrightarrow \text{  } \xrightarrow{+(20)} Ph{\cdot}Ph + \begin{array}{l} Ph{\cdot}N{\cdot}OH \\ \quad | \\ Ph{\cdot}N{\cdot}Ac \end{array}$$

$$Ph{\cdot}N{:}N{\cdot}O{\cdot}Ac + \begin{array}{l} Ph{\cdot}N{\cdot}OH \\ \quad | \\ Ph{\cdot}N{\cdot}Ac \end{array} \longrightarrow (20) + Ph\cdot + N_2 + AcOH$$

The details of the last step have not been defined, but a possible route is shown below:

$$Ph{\cdot}N{:}N{\cdot}OAc \rightleftharpoons Ph{\cdot}N_2^{+} + AcO^{-}$$

$$AcO^{-} + \begin{array}{l} Ph{\cdot}N{\cdot}OH \\ \quad | \\ Ph{\cdot}N{\cdot}Ac \end{array} \longrightarrow AcOH + \begin{array}{l} Ph{\cdot}N{\cdot}O^{-} \\ \quad | \\ Ph{\cdot}N{\cdot}Ac \end{array}$$

$$\begin{array}{l} Ph{\cdot}N{\cdot}O^{-} \\ \quad | \\ Ph{\cdot}N{\cdot}Ac \end{array} + PhN_2^{+} \longrightarrow \begin{array}{l} Ph{\cdot}N{\cdot}O{\cdot}N_2{\cdot}Ph \\ \quad | \\ Ph{\cdot}N{\cdot}Ac \end{array} \longrightarrow Ph\cdot + N_2 + (20)$$

These two schemes are obviously very similar, the chief difference lying in the nature of the chain-carrying radical. For convenience, therefore, Rüchardt's scheme is used in this Discussion whenever such a scheme is required. A clear decision between the two possible schemes will rest on a detailed analysis of the fine structure of the intermediate

radical, but in any event, neither scheme accommodates certain anomalous observations reported in the literature previously.

Accordingly, the work described in this thesis was carried out in an attempt to elucidate further the reactions of N-nitrosoacylarylamines in organic solvents. Since Cadogan and Hibbert (see p. 17 ) had shown that o- t-butyl-N-nitrosoacetanilide decomposed via an intermediate aryne, it was of interest to investigate the possibility that aryne intermediates might be involved in the reactions of N-nitrosoacylarylamines in general. It was felt that the use of an N-nitrosobenzanilide, which would give rise to the more easily detectable benzoic acid and anhydride, if the latter was formed, would lead to more useful results than an N-nitrosoacetanilide. Reactions of N-nitrosobenzanilides in organic solvents had not been systematically investigated before this study began.

## REACTIONS OF N-NITROSOBENZANILIDES IN AROMATIC SOLVENTS.

### I. Reaction in Chlorobenzene.

It was first necessary to establish the products of the reaction in aromatic solvents. Thus, 4-chloro-N-nitrosobenzanilide [$Ph{\cdot}N{\cdot}(NO){\cdot}CO{\cdot}C_6H_4Cl$ (-p)] on decomposition in chlorobenzene gave p-chlorobenzoic acid (95%) and a mixture of isomeric chlorobiphenyls (47%), the ratio o:m:p being 60:23:17. This ratio is similar to that ($62\pm3:24\pm3:14\pm3$) found in the phenylation of chlorobenzene using benzoyl peroxide and other known radical sources[12,13,151] indicating that the phenylation of chlorobenzene by N-nitrosobenzanilides is a radical process.

II. Reactions in Benzene.

The results of the reactions of substituted 4-chloro-N-nitroso-benzanilides [Ar·N(NO)·CO·$C_6H_4$Cl (-p)] with benzene are summarised in Table 7 (p.67 ).

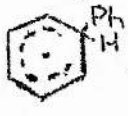
a) Reactions of Monosubstituted and Unsubstituted 4-chloro-N-Nitrosobenzanilides [R·$C_6H_4$·N·(NO)·CO·$C_6H_4$Cl(p)]

These reactions yield products analogous to those from the reaction of N-nitrosoacetanilide with benzene. Thus, in every reaction (R=H, o-Br, m-Br, p-Br, p-Me) the major product is p-chlorobenzoic acid (80-92%), with lower yields of the appropriate biphenyl (37-68%). Additional products are formed in only two reactions: bromobenzene (0.3%) is produced in the reaction of 4'-bromo-4-chloro-N-nitrosobenzanilide (R=p-Br) and phenyl 4-chlorobenzoate (1%) is formed in the reaction of 4-chloro-N-nitrosobenzanilide (R=H). It appears, therefore, that the reactions of N-nitrosobenzanilides in benzene follow a mechanism similar to that proposed[25,78,160] for the decomposition of nitrosoacetanilide, as shown: (Ar=p-Cl·$C_6H_4$·)

$$Ph\cdot N\cdot(NO)\cdot CO\cdot Ar \longrightarrow Ph\cdot N{:}N\cdot O\cdot CO\cdot Ar \rightleftharpoons PhN_2^{+} + Ar\cdot CO_2^{-}$$

$$Ph\cdot N{:}N\cdot O\cdot CO\cdot Ar + Ar\cdot CO_2^{-} \longrightarrow Ph\cdot N_2\cdot O^{-} + (Ar\cdot CO)_2\cdot O$$

$$Ph\cdot N_2\cdot O^{-} + Ph\cdot N_2^{+} \longrightarrow Ph\cdot N_2\cdot O\cdot N_2\cdot Ph \longrightarrow Ph\cdot + N_2 + Ph\cdot N_2\cdot O\cdot$$

$$Ph\cdot + PhH \longrightarrow \text{  } \xrightarrow{Ph\cdot N_2\cdot O\cdot} Ph\cdot Ph + Ph\cdot N_2\cdot OH$$

$$Ph\cdot N_2\cdot OH + Ar\cdot CO_2^{-} \longrightarrow Ar\cdot CO_2H + Ph\cdot N_2\cdot O^{-}$$

The presence of the other products (bromobenzene and phenyl 4-chlorobenzoate) may be accounted for by the formulation of additional

reaction schemes which can take place within the framework of those proposed by Rüchardt or Perkins.

The formation of phenyl 4-chlorobenzoate (p·Cl·$C_6H_4$·CO·O·Ph) may proceed via one of the following routes:

i) by the nucleophilic displacement by a 4-chlorobenzoate anion of nitrogen from the intermediate diazonium cation.

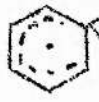
$$Ph{\cdot}N{:}N{\cdot}O{\cdot}CO{\cdot}Ar \longrightarrow PhN_2^{+} + Ar{\cdot}CO_2^{-} \longrightarrow Ar{\cdot}CO{\cdot}O{\cdot}Ph + N_2$$

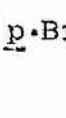
No esters are detected in reactions of the other monosubstituted nitrosoamides however, although the activating influence of a bromo substituent in the o- or p- positions [e.g. in o-Br·$C_6H_4$·N(NO)·CO·Ar] should facilitate such a displacement.

ii) by combination of radicals produced in the homolysis of the diazo ester, which may occur to a slight extent.

$$Ph{\cdot}N{:}N{\cdot}O{\cdot}CO{\cdot}Ar \longrightarrow Ph{\cdot} + Ar{\cdot}COO{\cdot} + N_2 \longrightarrow Ar{\cdot}CO{\cdot}O{\cdot}Ph + N_2$$

The formation of bromobenzene in the reaction of 4'-bromo-4-chloro-N-nitrosobenzanilide may be explained by abstraction of hydrogen from the cyclohexadienyl radical by a p-bromophenyl radical.

e.g. p·Br·$C_6H_4$· + PhH ⟶  $C_6H_4Br$ (-a)



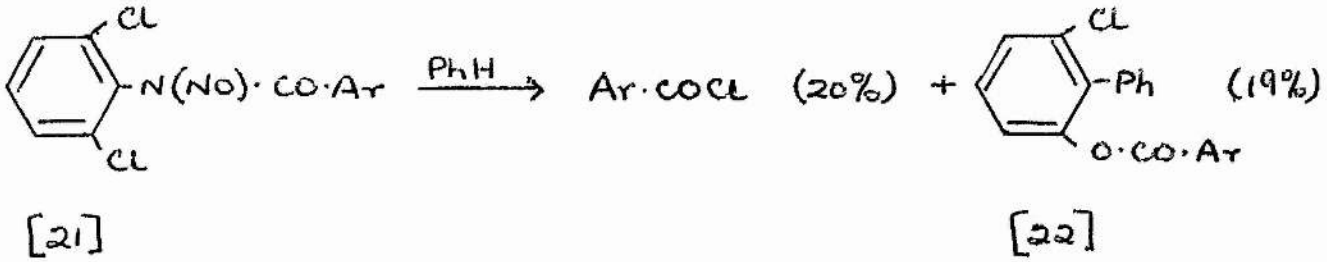
p·Br·$C_6H_4$·

p·Br·$C_6H_4$·Ph + PhBr

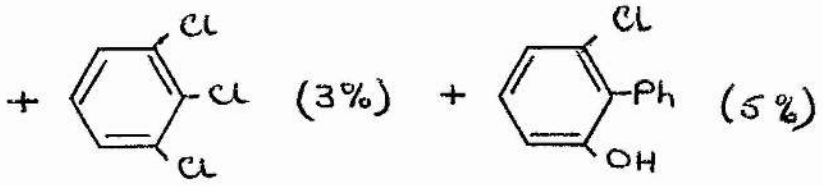
There are no products analogous to bromobenzene formed in the reactions of the other mono-substituted N-nitrosoamides, however.

## Equation 1

(Ar = p-Cl·C$_6$H$_4$-)




[21] [22]




[23]

+ Ar·CO$_2$H (5%) + (Ar·CO)$_2$O (3%)

The products of the reactions of mono-substituted N-nitrosobenzanilides can thus be adequately explained by the schemes previously proposed by Rüchardt and by Perkins.

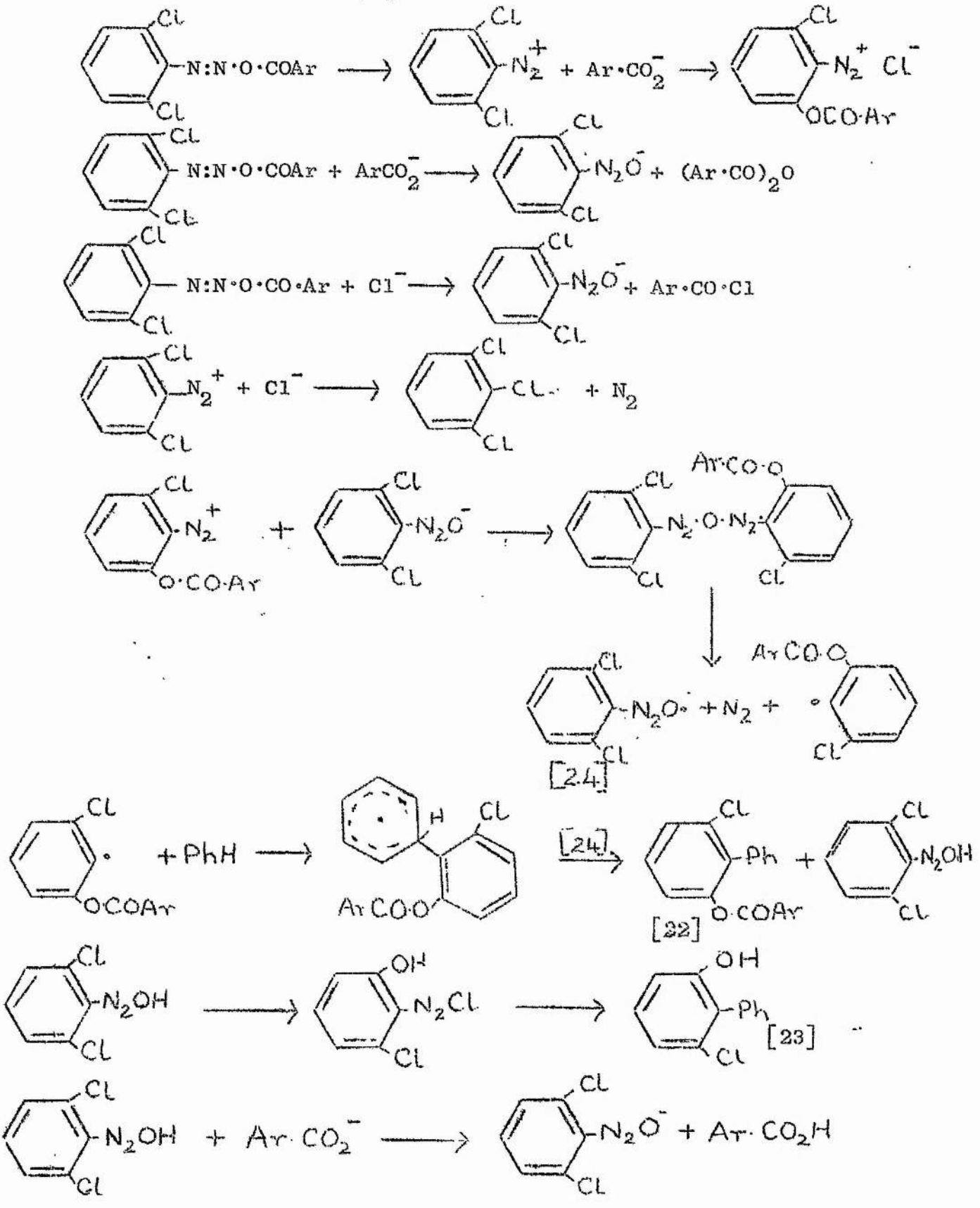
b) Reactions of o-Disubstituted N-Nitrosobenzanilides with Benzene.

When both o-positions in the amino moiety of the nitrosoamide are substituted, however, the reaction appears to take a different course. The products of the reaction of 2',4,6'-trichloro-N-nitrosobenzanilide [21] are shown in Equation 1 opposite. In this case, very little p-chlorobenzoic acid (5%) is produced, and the major products are p-chlorobenzoyl chloride (20%) and 2-chloro-6-(p-chlorobenzoyloxy)-biphenyl [22] (19%), with smaller amounts of 1,2,3-trichlorobenzene (3%), 2-chloro-6-hydroxybiphenyl [23] (5%) and p-chlorobenzoic anhydride (3%).

Isolation of p-chlorobenzoic anhydride from this reaction is the first indication that Rüchardt's and not Perkins' scheme may be operative, and is in accordance with Suschitzky's suggestion[160] that benzoic anhydride is produced in the reaction of N-nitrosobenzanilide with benzene. In the present investigation, however, carboxylic anhydrides have been detected in the reaction of 2',4,6'-trichloro-N-nitrosobenzanilide only, and not in the reactions of mono-substituted N-nitrosobenzanilides with benzene.

The yield of p-chlorobenzoic acid is unusually low for any of the previously proposed schemes to be operative. From the structure of the biphenyl ester [22] it is evident that one of the o-substituents has been replaced, possibly by nucleophilic attack of a benzoate anion.

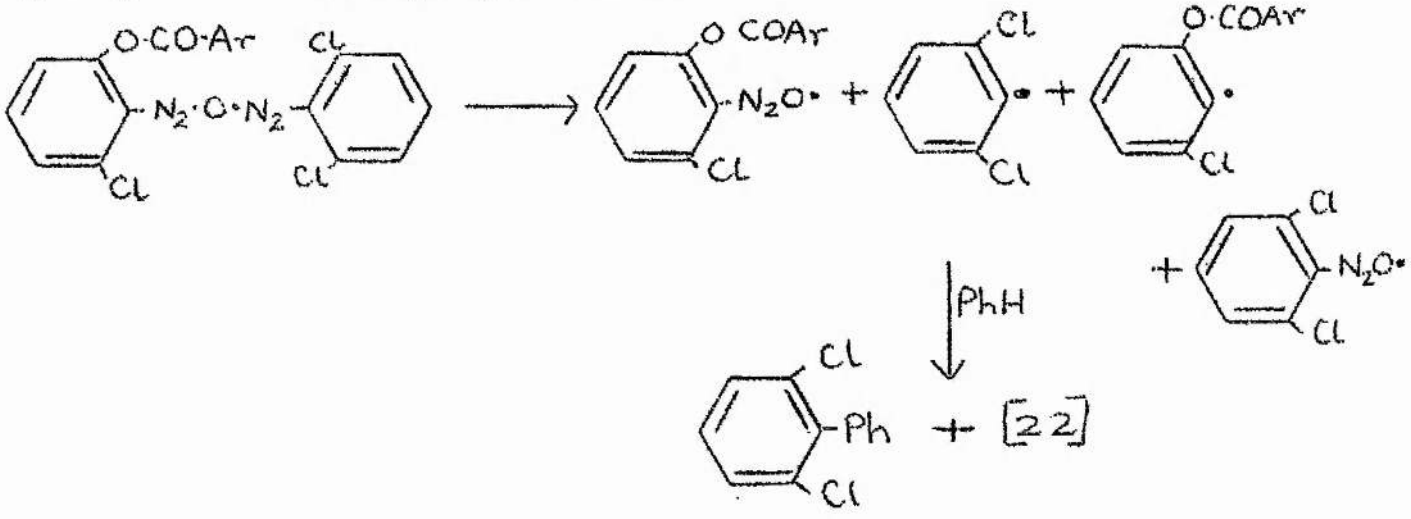
A modification of Richardt's scheme, as shown below, can account for all the products. [Ar = p-Cl·C$_6$H$_4$·]



The low yield of acid may be accounted for if the 4-chlorobenzoate ion ($Ar \cdot CO_2^-$) displaces the chlorinefrom the diazonium cation rather than abstracts a proton from the intermediate diazohydroxide ($Ar \cdot N_2OH$).

The phenol [23] is not produced by hydrolysis of the corresponding ester [22], since control experiments showed the ester to be stable under the reaction conditions.

There is, however, one drawback to this scheme. The diazoanhydride shown should be capable of homolysis in two positions, giving rise to two biphenyls as shown:




However, no 2,6-dichlorobiphenyl is detected in this reaction, suggesting that an intermediate diazoanhydride of this type is not involved in the reaction. Further work will be necessary to solve this problem.

The detection of 1,2,3-trichlorobenzene in the reaction suggests the presence of free chloride ions. Such halogen displacement is well established. Thus, Hantzsch and Smythe[152] have found that substituted o-bromobenzenediazonium chlorides readily rearrange to the corresponding o-chlorobenzenediazonium bromides. Also, attack by a benzoate ion would be similar to that demonstrated by Suschitzky[72,73] in reactions of

o- and p-fluoro-N-nitrosoacylarylamines, but in that case the reaction has been attributed to the enhanced electronegativity of the fluorine. The absence of the corresponding benzoyloxybiphenyls ($Ar \cdot CO \cdot O \cdot C_6H_4 \cdot Ph$) in reactions of 2'-bromo and 4'-bromo-4-chloro-N-nitrosobenzanilides [i.e. $o\text{-}Br \cdot C_6H_4 \cdot N(NO) \cdot COAr$ and $p \cdot Br \cdot C_6H_4 \cdot N(NO)COAr$] seems to add support to Suschitzky's results that halogens other than fluorine are not replaced in monohalogeno compounds. In the present case, where there is a chloro substituent in both o-positions in the amino moiety in the molecule, there is presumably sufficient activation for one of the halogens to be displaced (c f. Ref. 164). The blocking of both o-positions, however, may cause the reaction to proceed via a pathway not previously preferred, i.e. elimination of a halogen rather than formation of the carboxylic acid, because this is the only course now possible.

Thus, apart from this case, there are obvious similarities between the decompositions of N-nitrosoacetanilides and N-nitrosobenzanilides, and there is no evidence even to suspect the intermediacy of an aryne. There is, however, one observation which seems to suggest that N-nitrosoacetanilides and N-nitrosobenzanilides do not decompose by the same mechanism in benzene. The decompositions of N-nitrosoacetanilide and p-chloro-N-nitrosoacetanilide [$p \cdot Cl \cdot C_6H_4 \cdot N(NO) \cdot Ac$] give E.S.R. spectra which can be attributed to the phenyldiazotate radical ($Ph \cdot N_2O \cdot$) and the 4-chlorophenyldiazotate radical ($p \cdot Cl \cdot C_6H_4 \cdot N_2O \cdot$) respectively (c.f. Ref. 75). However, 4-chloro-N-nitrosobenzanilide

[Ph·N(NO)·CO·$C_6H_4Cl(p)$] in benzene shows only a weak, unresolvable signal, which is not that shown by N-nitrosoacetanilide. It may be that the nitrogen and the p-chlorobenzoic acid which are formed in the reaction interfere mechanically with the production of the spectrum. Alternatively, the reaction may be so fast that the presence of the radical is unnoticed. This is unlikely, however, since attempts to produce a spectrum have been made with the reaction mixture initially cooled to -20°C.

III. Reactions of N-Nitrosoacylarylamines in Carbon Tetrachloride.

a) Reactions of N-Nitrosoacetanilide.

The decomposition of N-nitrosoacetanilide in carbon tetrachloride has been reported[1,28,29,30,34] to give benzenediazonium chloride as an intermediate and to yield chlorobenzene and acetic acid, but no hexachloroethane. No mechanism for the decomposition in carbon tetrachloride has been proposed. This reaction has now been re-investigated and has been found to proceed in two stages. At room temperature, nitrogen (45% of the theoretical amount) is evolved, leaving benzenediazonium chloride, chlorobenzene and acetic acid. On being warmed to 40°C, the diazonium salt decomposes with the elimination of nitrogen (a further 35% of the theoretical total value) to give the final products, acetic acid (54%), chlorobenzene (33%), and phenyl acetate (5%). Evidence for acetic anhydride (15%) comes from the I.R. spectrum of a distillation fraction, from the formation of acetanilide on the addition of aniline to this fraction, and from the titration figures (see p. 93) before and after the addition of aniline.

## Equation 2

$$R\cdot C_6H_4\cdot N(NO)\cdot CO\cdot Ar \xrightarrow{CCl_4} Ar\cdot CO_2H + (Ar\cdot CO)_2O$$

$$+ R\cdot C_6H_4\cdot Cl + R\cdot C_6H_4\cdot O\cdot CO\cdot Ar$$

The presence of acetyl chloride in a second distillation fraction is suggested by the smell, the acidic fumes and the production of acetanilide on the addition of aniline to this fraction. Hydrogen chloride (<5%) must also be present since aniline hydrochloride is produced. Phosgene has been detected by phosgene test-paper, but no N,N'-diphenylurea has been isolated from an aqueous aniline trap.

The E.S.R. spectrum of N-nitrosoacetanilide in carbon tetrachloride is entirely different from that in benzene. In this case, a triplet of triplets is obtained, but this is so weak and disappears so quickly that it cannot be resolved. Nitrosoacetanilide therefore appears to decompose by different mechanisms in benzene and in carbon tetrachloride.

b) Reactions of Substituted 4-Chloro-N-Nitrosobenzanilides.

$$[R \cdot C_6H_4 \cdot N(NO) \cdot CO \cdot C_6H_4Cl(p)]$$

The products from the reaction of the unsubstituted (R=H) and mono-substituted (R=o-Br, m-Br, p-Br, p-Me, p-$NO_2$) nitrosobenzanilides in carbon tetrachloride again parallel those from the reaction of N-nitrosoacetanilide (see Equation 2), and they are summarised in Table 8 (p. 78). One of the important products in these reactions is p-chlorobenzoic acid (29-72%), which, in this solvent, cannot have arisen by the schemes proposed by Rüchardt or Perkins. p-Chlorobenzoic anhydride, as required by Rüchardt's mechanism, is also produced, but in much smaller yields (6-19%).

Another feature of these reactions is the formation of aryl halides. Those formed from the reaction of compounds containing bromine or a nitro group in the o- or p-position in the amino moiety show replacement of the substituent by chlorine. [Ar = p·Cl·$C_6H_4$·]

e.g. p·Me·$C_6H_4$·N(NO)·COAr ⟶ p·Me·$C_6H_4$Cl (25%)

but p·$NO_2$·$C_6H_4$·N(NO)·COAr ⟶ p·$NO_2$·$C_6H_4$·Cl (32%) + p·Cl·$C_6H_4$·Cl (2%)

and o-Br·$C_6H_4$·N(NO)·COAr ⟶ o·Br·$C_6H_4$·Cl (15%) + o·Cl·$C_6H_4$·Cl (12%) + o·Br·$C_6H_4$·Br (11%).

This displacement of bromine and a nitro group by chlorine is noticeable also in the formation of substituted phenyl 4-chlorobenzoates in these reactions.

e.g. p·Me·$C_6H_4$·N(NO)·COAr ⟶ p·Me·$C_6H_4$·O·COAr (0.5%)

but p·$NO_2$·$C_6H_4$·N(NO)·COAr ⟶ p·Cl·$C_6H_4$·O·COAr (11%)

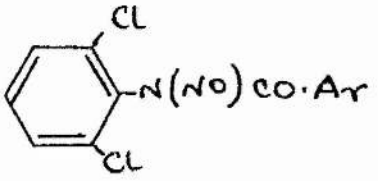
and p·Br·$C_6H_4$·N(NO)·COAr ⟶ p·Br·$C_6H_4$·O·COAr (1%) + p·Cl·$C_6H_4$·O·COAr (c%)

The yield of ester appears to depend on the substituent present. Compounds with m-substituents [e.g. m·Br·$C_6H_4$·N(NO)·COAr] and those with an electron releasing group in the p-position [e.g. p·Me·$C_6H_4$·N(NO)·COAr] give very low yields of ester (<<1%).

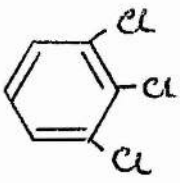
When both o-positions in the amino moiety of the nitrosoamide are substituted, the reaction takes a different course. The products of the reactions of 2',4,6'-trichloro- and 4-chloro-2',4',6'-tribromo-N-nitrosobenzanilide with carbon tetrachloride are detailed in Table 9 (p.85 ). The major product of the reaction of 2',4,6'-trichloro-N-nitrosobenzanilide is p-chlorobenzoyl chloride (45%) [see Equation 3],

## Equation 3

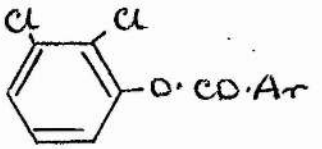
(Ar = p-Cl·C$_6$H$_4$-)




$\xrightarrow{CCl_4}$ Ar·COCl (45%) + Ar·CO$_2$H (2%)

+ (Ar·CO)$_2$O (0.5%) + 

(4%)

+ 

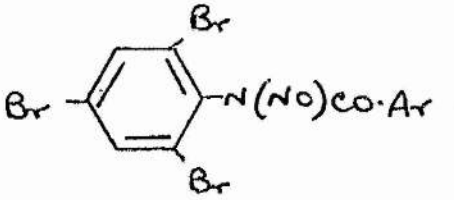
(3%)

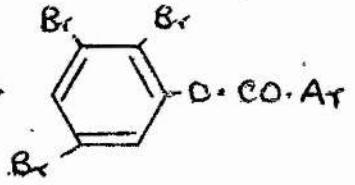
[25]

---

## Equation 4

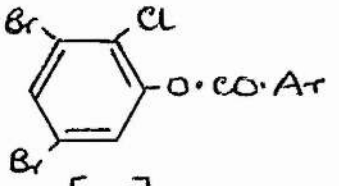
(Ar = p-Cl·C$_6$H$_4$-)




$\xrightarrow{CCl_4}$ 

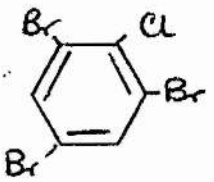
(21%) + Ar·CO$_2$H (2%)

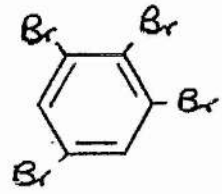
[26]

+ 

(4%) + Ar·COCl (1%)

[27]

+ 

(0.7%) + 

(2%)

with smaller amounts of p-chlorobenzoic acid (2%), p-chlorobenzoic anhydride (0.5%), 1,2,3-trichlorobenzene (4%) and 2,3-dichlorophenyl 4-chlorobenzoate [25] (3%). An unidentified brown solid is produced in this reaction in considerable amount.

In the reaction of 4-chloro-2',4',6'-tribromo-N-nitrosobenzanilide [see Equation 4] the major product is 2,3,5-tribromophenyl 4-chlorobenzoate [26] (21%), but also formed are p-chlorobenzoic acid (2%), 2-chloro-3,5-dibromophenyl 4-chlorobenzoate [27] (4%), p-chlorobenzoyl chloride (1%), 1-chloro-2,4,6-tribromobenzene (0.7%) and 1,2,3,5-tetrabromobenzene (2%).

By comparison of Equations 2,3 and 4, it is clear that, when both o-positions in the amino moiety are substituted, the formation of acid, acid anhydride and aryl halides is suppressed, and the formation of acid chloride or esters predominates.

Each of these products will now be discussed in detail.

1. Formation of p-Chlorobenzoic Acid.

The decomposition of 4-chloro-N-nitrosobenzanilide [$Ph{\cdot}N(NO){\cdot}CO{\cdot}C_6H_4{\cdot}Cl(p)$] in carbon tetrachloride yields, as the major product, p-chlorobenzoic acid (45%). That the acid is a primary product is shown by the fact that neither p-chlorobenzoyl chloride nor p-chlorobenzoic anhydride is hydrolysed to the acid under the reaction conditions. Since both schemes previously proposed depend on the solvent to supply hydrogen for the formation of the acid, the acid produced in the reaction with carbon tetrachloride must arise by some other mechanism, the acidic hydrogen originating in the nitrosoamide itself.

The yields of carboxylic acid formed from the reactions of substituted N-nitrobenzanilides with carbon tetrachloride are shown in Table 13.

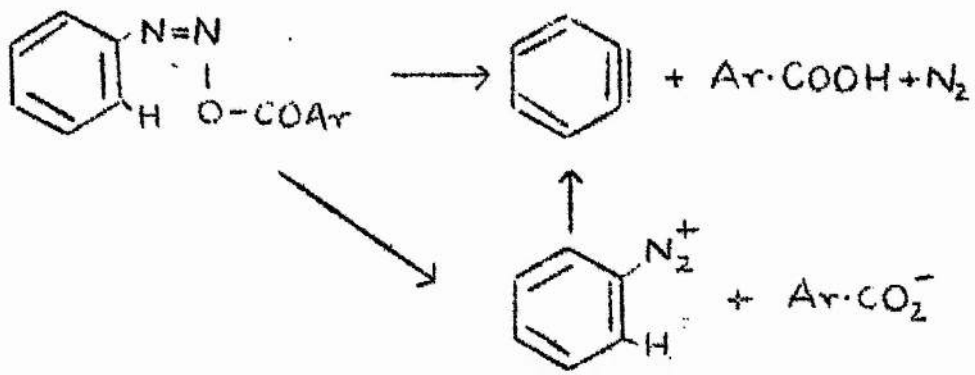
Table 13

| | Ar=p·Cl·$C_6H_4$· | | | | | | | Ar=p·Br·$C_6H_4$ | |
|---|---|---|---|---|---|---|---|---|---|
| R in $R·C_6H_4N(NO)·COAr$ | p-$NO_2$ | p-Br | p-Me | o-Br | m-Br | 2,6 diCl | 2,4,6 triBr | p·$NO_2$ | p-Br |
| Yield (%) of Ar·COOH | 68 | 49 | 79 | 29 | 57 | 2 | 2 | 65 | 40 |

It is apparent that acid is produced as the major product in reactions of all N-nitrosobenzanilides except those in which both o-positions in the amino moiety are substituted. A similar effect has already been observed in benzene. It would therefore appear that the o-position in the amino moiety is the origin of the acidic hydrogen, although, by having two o-substituents in the one molecule, the reaction path may have been altered considerably. It may be that a reaction which is not generally preferred (e.g. elimination of a substituent) is forced to occur in preference to the formation of p-chlorobenzoic acid by abstraction of hydrogen.

Since Cadogan and Hibbert had shown (see p. 17) that, in the reaction of o-t-butyl-N-nitrosoacetanilide with benzene, the o-hydrogen was removed in the formation of acetic acid, giving an intermediate aryne, it was felt that a similar mechanism might be operative here, even without the influence of the bulky o-t-butyl group.

i.e.




Experiments were therefore designed to trap any intermediate aryne which might be present, using known aryne traps. The results of these experiments will be discussed later (see p.157).

2. Formation of Acid Anhydrides.

p-Bromobenzoic anhydride (13-17%) has been isolated from reactions of substituted 4-bromo-N-nitrosobenzanilides [Ar·N(NO)·CO·$C_6H_4$·Br(-p)] in carbon tetrachloride (see Table 10, p. 90). Similarly, p-chlorobenzoic anhydride (1-19%) has been isolated from reactions of substituted 4-chloro-N-nitrosobenzanilides [Ar·N(NO)·CO·$C_6H_4$Cl(p)] [Table 8, p. 78], the yields depending on the position of substituents in the amino moiety. Very low yields of anhydride are found in the reactions of compounds having substitutents in both o-positions in the amino moiety [e.g. 2',4,6'-trichloro-N-nitrosobenzanilide] [see Table 9, p. 85], presumably because, as has been already suggested, the reaction prefers to take a different course in such cases. There is also evidence for the formation of acetic anhydride (15%) in the reaction of N-nitrosoacetanilide with carbon tetrachloride.

The isolation or detection of carboxylic anhydrides in such reactions has not been reported previously, although Suschitzky has recently suggested that benzoic anhydride is produced in the reaction of nitrosobenzanilide with benzene. Their presence is in accord with the reaction scheme proposed by Rüchardt, i.e. attack of a benzoate anion on the diazo ester.

e.g. $Ar\cdot N(NO)\cdot COAr' \longrightarrow Ar\cdot N{:}N\cdot O\cdot COAr' \longrightarrow ArN_2^+ + Ar'CO_2^-$

$Ar\cdot N{:}N\cdot O\cdot COAr' + Ar'CO_2^- \longrightarrow Ar.N_2O^- + (Ar'\cdot CO)_2O$

The formation of acid anhydrides by Suschitzky's modified scheme is also possible:

$ArN(NO)\cdot COAr' \longrightarrow Ar\cdot N_2O^- \; Ar'\overset{+}{C}O \longrightarrow Ar\cdot N{:}N\cdot O\cdot COAr' \rightleftharpoons Ar.N_2^+ \; Ar'\cdot CO_2^-$

$Ar'\cdot\overset{+}{C}O + Ar'\cdot CO_2^- \longrightarrow (Ar'CO)_2O$

The reaction cannot proceed in carbon tetrachloride as proposed in these schemes, however, since no acid formation would be possible in this solvent.

3. Formation of Aryl Halides.

Aryl halides are among the major products of all reactions of N-nitrosobenzanilides in carbon tetrachloride, apart from those in which both o-positions in the amino moiety are substituted (see Tables 8,9,10, pp. 78,85,90 ). In the decomposition of nitrosoamides having bromine or a nitro group in the o- or p- position in the amino moiety [e.g. $p\cdot Br\cdot C_6H_4\cdot N(NO)CO\cdot Ar$] aryl halides are formed in which the substituent has been replaced by chlorine, as shown in Table 14.

Table 14

Yield (%) of Aryl Halides from Ar·N(NO)·CO·Ar'[Ar'=p·Cl·$C_6H_4$-]

| Ar in Ar·N(NO)·COAr' | ArCl | ArBr | p·Cl·$C_6H_4$Cl | m·Cl·$C_6H_4$Cl | o·Cl·$C_6H_4$Cl |
|---|---|---|---|---|---|
| Ph | 26 | - | - | - | - |
| p·Me·$C_6H_4$ | 20 | - | - | - | - |
| p·$NO_2$·$C_6H_4$ | 32 | - | 2 | - | - |
| p·Br·$C_6H_4$ | 26 | 5 | 25 | - | - |
| m·Br·$C_6H_4$ | 32 | 2 | - | 1 | - |
| o-Br·$C_6H_4$ | 15 | 11 | - | - | 12 |
| 2,6-diCl·$C_6H_3$ | 4 | - | - | - | - |
| 2,4,6-triBr·$C_6H_2$ | 0.7 | 2 | - | - | - |

Since the phenylation of chlorobenzene by N-nitrosobenzanilides has been shown to be a radical process, it is possible that radicals may also be present as intermediates in reactions in carbon tetrachloride. In this connection, the observation of an E.S.R. signal in this system indicates the presence of radicals, but in unknown concentration. Aryl halides would thus occur by abstraction of chlorine from the carbon tetrachloride by an aryl radical.

i.e. Ar·N(NO)·COAr' $\longrightarrow$ Ar· $\xrightarrow{CCl_4}$ ArCl + ·$CCl_3$.

The trichloromethyl radicals thus formed would be expected to dimerise, giving hexachloroethane. No trace of this dimer has been found by G.L.C. in any of the reactions, however, and none has been isolated, which seems to suggest that formation of the aryl halide may not be a radical process. The trichloromethyl radical may, however, be

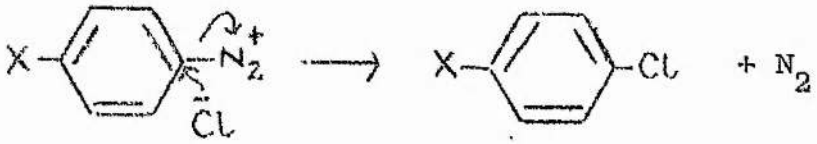
scavenged by some other, more stable radical, e.g. $Ph\cdot N_2\cdot O\cdot$ which can lead to $Ph\cdot N{:}N\cdot O\cdot CCl_3$. Presumably this would decompose to chlorobenzene, nitrogen and phosgene. Phosgene has been shown to be present in some of the reactions, but the yield is probably very low as no N,N'-diphenylurea has been isolated by reaction with aniline. Scavenging in this reaction would be similar to the reaction of phenylazotriphenylmethane with carbon tetrachloride,[123] where the absence of hexachloroethane is attributed to the scavenging of the trichloromethyl radical by the more stable triphenylmethyl radical. Alternatively, the trichloromethyl radical may be incorporated into the residue, which has been shown by sodium fusion to contain both nitrogen and chlorine.

The absence of the dimer, however, may be explained, quite simply, if the aryl halide formation is not radical at all, but ionic. There may be, in the reaction, an intermediate carbonium ion $Ar^+$. Such an intermediate has been proposed by Franck and Yanagi[161] in the decomposition of 2,5-di-t-butyl-N-nitrosoacetanilide where the bulky o- group is said to be responsible for the rapid elimination of nitrogen from the diazonium cation. In the present case, there is no such motivation for expulsion of the nitrogen, however.

Attack of a carbonium ion on carbon tetrachloride can lead to an aryl halide and a trichloromethyl cation which would not be expected to dimerise, but which may take part in further reaction.

i.e. $Ar\cdot N(NO)\cdot COAr' \longrightarrow Ar^+ \xrightarrow{CCl_4} ArCl + \dot{C}Cl_3$

A third possible method for the formation of the aryl halide involves the intermediate diazonium chloride, which has been shown to be present in reactions of N-nitrosoacylarylamines in carbon tetrachloride. The diazo group is readily displaced by nucleophilic attack of a halide ion.[162] In this reaction, the following reaction can therefore be expected to occur:



A higher yield of aryl halide is then to be expected if X is electron withdrawing (e.g. X=$NO_2$ ) than if X is electron releasing (e.g. X=Me ). This is borne out in practice (Table 14, p.143).

The diazonium chloride may be produced by one of the following methods:

(i) By one electron transfer from a trichloromethyl radical to a diazonium salt.

$$^{\bullet}CCl_3 + (ArN_2^{+} + Ar'CO_2^{-}) \longrightarrow Ar^{\bullet}N_2^{+}\ \bar{C}Cl_3 + Ar'^{\bullet}CO_2^{\bullet}$$

$$ArH_2 + \bar{C}Cl_3 \longrightarrow ArN_2^{+}Cl^{-} + :CCl_2$$

However, no products from further reaction of the acetoxy radical (especially carbon dioxide) have been found, and previous attempts by Hibbert[34] to trap dichlorocarbene in a similar reaction of N-nitrosoacetanilide have been unsuccessful.

(ii) By abstraction of a chloride ion from the carbon tetrachloride by a diazonium cation.

e.g. $Ph^{\bullet}N_2^{+} + CCl_4 \longrightarrow Ph^{\bullet}N_2^{+}Cl^{-} + \dot{C}Cl_3$

(iii) By the scavenging action of the phenyl diazotate radical.

e.g. $Ph\cdot N_2\cdot O\cdot + \cdot CCl_3 \longrightarrow Ph\cdot N_2\cdot O\cdot CCl_3$

$$\downarrow$$

$$Ph\cdot N_2^+ Cl^- + COCl_2$$

Since phosgene has been detected in certain reactions, this may be the method of production of the diazonium chloride. However, the experiments carried out in this investigation do not allow a decision over the genesis of the diazonium chloride to be made.

There are thus three possible modes of formation of the aryl halide:

$$Ar\cdot + CCl_4 \longrightarrow ArCl + \cdot CCl_3$$

$$Ar^+ + CCl_4 \longrightarrow ArCl + \dot{C}Cl_3$$

$$Ar\cdot N_2^+ Cl^- \longrightarrow ArCl + N_2 \quad ,$$

all of which may take place simultaneously.

The multiplicity of aryl halides produced in the reactions of nitrosoamides having a bromo or a nitro substituent (see Tabl 14, p. 143) can be rationalised on the basis of the intermediate diazonium chloride. Hantzsch and Smythe[152] have reported that substituted o- and p-bromobenzenediazoniumchlorides rearrange to the corresponding o- and p-chlorobenzenediazonium bromides, the o-substituent being more readily replaced than the p-substituent, and the m-substitutent showing no exchange. Hey et al.[14] have reported a similar bromine-chlorine exchange on the passage of hydrogen chloride through a solution of 1-p-bromophenyl-3,3-dimethyltriazene. It is therefore reasonable to

assume that a similar rearrangement occurs in the intermediate diazonium chloride in the present reaction.

e.g. $\underline{p}\cdot Br\cdot C_6H_4N_2^+Cl^- \longrightarrow \underline{p}\cdot Cl\cdot C_6H_4N_2^+Br^-$

Such a rearrangement leads to the presence of both chloride and bromide ions in the solution, and both of these can attack either or both of the diazonium cations, yielding a mixture of aryl halides, as shown:

$\underline{p}\cdot Br\cdot C_6H_4N_2^+Cl^- \longrightarrow \underline{p}\cdot Cl\cdot C_6H_4N_2^+Br^-$

$\underline{p}\cdot Br\cdot C_6H_4N_2^+ + Cl^- \longrightarrow \underline{p}\cdot Br\cdot C_6H_4\cdot Cl + N_2$

$\underline{p}\cdot Br\cdot C_6H_4N_2^+ + Br^- \longrightarrow \underline{p}\cdot Br\cdot C_6H_4Br + N_2$

$\underline{p}\cdot Cl\cdot C_6H_4N_2^+ + Cl^- \longrightarrow \underline{p}\cdot Cl\cdot C_6H_4\cdot Cl + N_2$

$\underline{p}\cdot Cl\cdot C_6H_4N_2^+ + Br^- \longrightarrow \underline{p}\cdot Cl\cdot C_6H_4Br + N_2$

p-Bromochlorobenzene may thus be formed in two ways.

The rearrangements in other reactions will occur in a similar way. The diazo group activates the o-position more than the p-position,[162] and so the rearranged aryl halides would be expected to constitute a greater percentage of the total aryl halide in the reaction of o-substituted nitrosoamides than in the reaction of p-substituted nitrosoamides. This is borne out in practice, as shown in Table 14 (p. 143). There is very little exchange with a m- substituent or where the substituent is a nitro group. This agrees with the results of Hantzsch and Smythe.

The free bromide ions may be responsible for the trace of bromine thought to be present in reactions of nitrosoamides having a bromo

substituent in the amino moiety [e.g. p·Br·$C_6H_4$·N(NO)·CO·Ar]. Similarly, the brown fumes observed in reactions of nitro-substituted compounds [p-$NO_2$·$C_6H_4$·N(NO)·CO·Ar] may originate in the displaced nitrite ions.

A further point to note about the halogen exchange reaction arises from reactions of substituted 4-bromo-N-nitrosobenzanilides [R·$C_6H_4$N(NO)·CO·$C_6H_4$Br·(p)] in carbon tetrachloride (see Table 10, p. 90). In the reaction of 4-bromo-4'-nitro-N-nitrosobenzanilide (R=p-$NO_2$) not only is there formed p-chloronitrobenzene (38%) and p-dichlorobenzene (2%), but also p-bromonitrobenzene (1%) and p-bromochlorobenzene (0.2%). The bromide ion for the halogen exchange must, in this case, come from the acyl group in the nitrosoamide, thus suggesting that tne following reaction has occurred:

$$Ar\cdot N{:}N\cdot O\cdot CO\cdot C_6H_4Br + Cl^- \longrightarrow Ar\cdot N{:}N\cdot O\cdot CO\cdot C_6H_4Cl + Br^-$$

However, no products corresponding to the nitrosoamide Ar·N(NO)·CO·$C_6H_4$Cl have been isolated, so that the evidence for such an exchange cannot be said to be conclusive.

4. Formation of Esters.

Esters (substituted phenyl 4-chlorobenzoates) are found in every reaction in carbon tetrachloride, but the yields depend on the nature and position of the substituents in the amino moiety of the nitrosoamide (See Table 8,9,10, pp.76,85,90 ]. In reactions of compounds having a bromo or nitro substituent in the o or p- position of the amino moiety, displacement of the substituent by chlorine is again apparent, as shown in Table 15.

Table 15 [Ar' = p·Cl·$C_6H_4$]

Ph·N(NO)·COAr' ⟶ Ph·O·COAr' (18%)

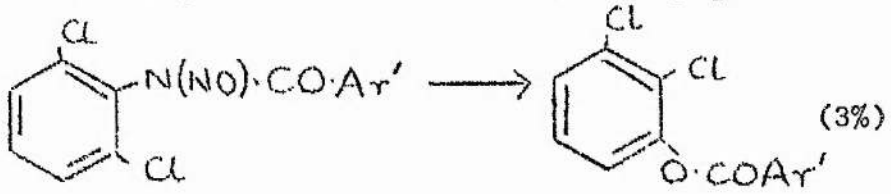
p·Me·$C_6H_4$·N(NO)·COAr' ⟶ p·Me·$C_6H_4$·O·COAr' (0.5%)

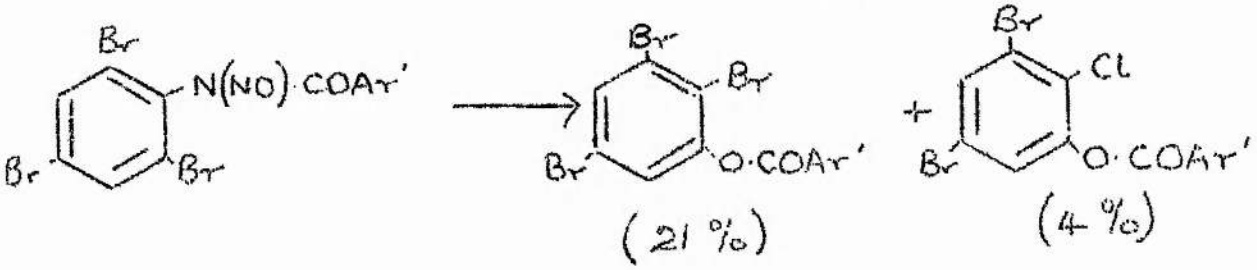
m·Br·$C_6H_4$·N(NO)·COAr' ⟶ m·Br·$C_6H_4$·O·COAr' (0.3%)

p·Br·$C_6H_4$·N(NO)·COAr' ⟶ p·Br·$C_6H_4$·O·COAr' (1%) + p·Cl·$C_6H_4$·O·COAr' (6%)

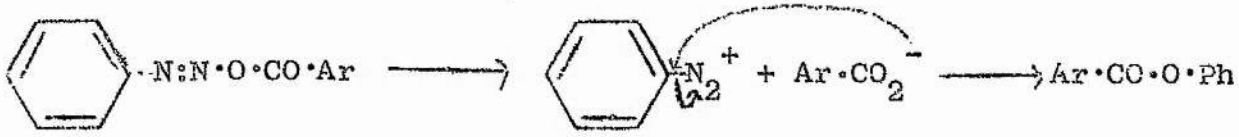
o·Br·$C_6H_4$·N(NO)·COAr' ⟶ o·Cl·$C_6H_4$·O·COAr' (1%)

p·$NO_2$·$C_6H_4$·N(NO)·COAr' ⟶ p·Cl·$C_6H_4$·O·COAr' (11%)

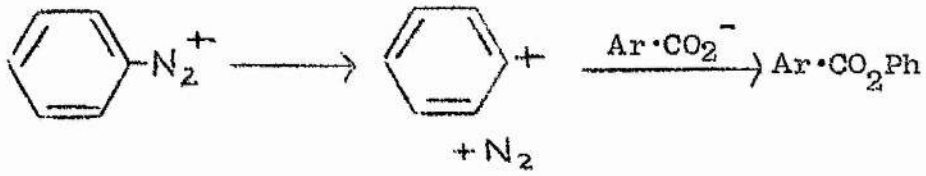



It can be seen that compounds containing a m-substituent or an electron-donating substitutent in the p-position [e.g. p·Me·$C_6H_4$·N(NO)·COAr'] give very low yields of ester and show no displacement by chlorine. The simple esters [i.e. Ar·N(NO)·CO·Ar' ⟶ Ar·O·COAr'] formed in these and the other reactions may be produced by elimination of nitrogen from the intermediate diazonium cation by the attack of a benzoate ion, as shown:

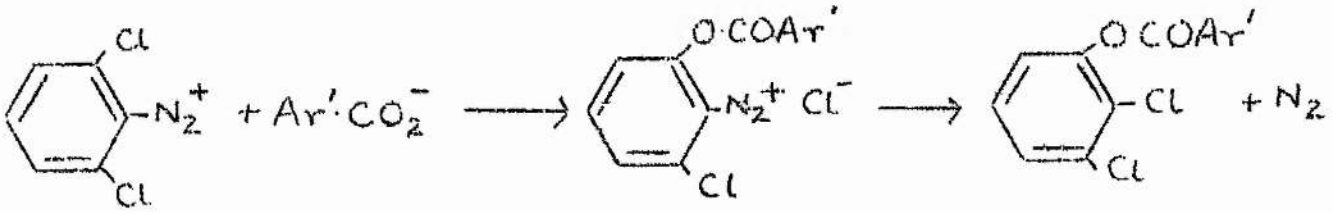


Alternatively, the benzoate ion may attack a carbonium ion, which has already been shown to be a possible intermediate (see. p. 144):

i.e. 

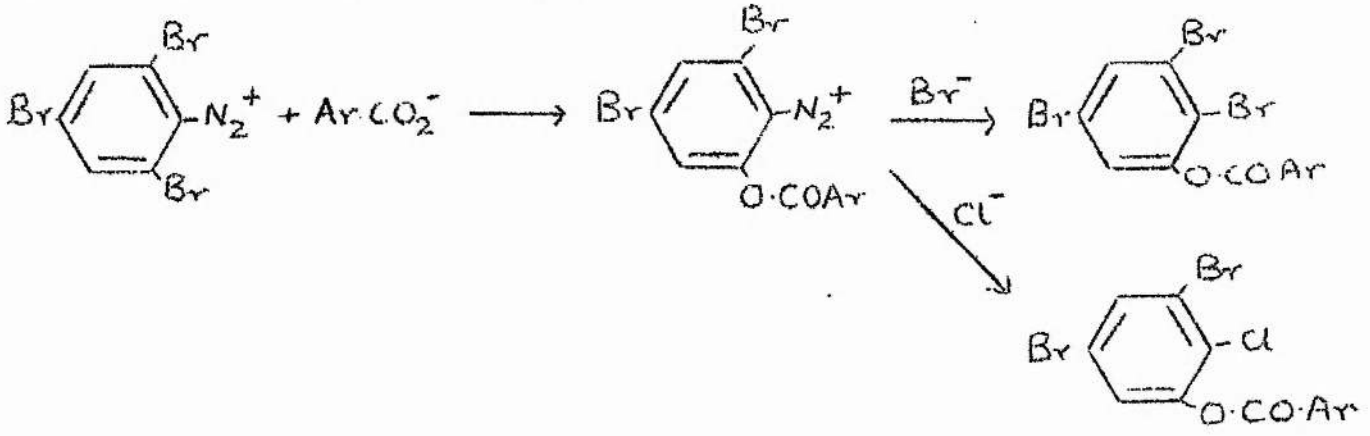
Because of the activating influence of electron withdrawing groups (e.g. $-NO_2$, -Br) on nucleophilic displacement,[163] compounds containing such groups [e.g. p·Br·$C_6H_4$N(NO)·CO·Ar] in the o- or p- position should yield more ester than those with electron-donating groups as substitutents. This is borne out in practice, as seen from Table 15, (p. 149).

In the reactions of compounds with substituents in both o-positions in the amino moiety of the nitrosoamide [e.g. 2',4,6'-trichloro-N-nitrosobenzanilide] it is postulated that one of the more easily accessible o-substituents, and not the hindered diazo group, is replaced as a result of the nucleophilic attack of a benzoate anion, giving rise to rearranged esters (see Table 15, p.149). The reaction of 2',4,6'-trichloro-N-nitrosobenzanilide would then proceed as shown:



The chlorine may be incorporated into the molecule by nucleophilic displacement of the diazo group by the chloride ion, or, alternatively, by homolysis of the diazo compound followed by abstraction from the carbon tetrachloride.

In the reaction of 4-chloro-2,'4',6'-tribromo-N-nitrosobenzanilide, the o-bromo and not the p-bromo substitutent is replaced, showing again the readiness of o-substituents to exchange. Chloride ions (from the diazonium chloride) will also be present in the solution and so a mixture of products will result, as shown:




A similar type of displacement appears to be operative in reactions of compounds having a bromo or a nitro substituent in the o- or p-position in the amino moiety (see Table 15, p.149). This displacement may occur by preliminary halogen exchange in the diazonium chloride

e.g.

$$\underline{p}\cdot Br\cdot C_6H_4\cdot N_2^+Cl^- \longrightarrow \underline{p}\cdot Cl\cdot C_6H_4N_2^+ \xrightarrow{Ar\cdot CO_2^-} \underline{p}\cdot Cl\cdot C_6H_4\cdot O\cdot COAr$$

However, it is more likely to occur by nucleophilic displacement of the substituent by a benzoate anion, as already described.

e.g. $\underline{p}\text{-}Br\cdot C_6H_4N_2^+ ArCO_2^- \longrightarrow Ar\cdot CO\cdot O\cdot C_6H_4N_2^+ \xrightarrow{Cl^-} Ar\cdot CO\cdot O\cdot C_6H_4Cl(\underline{p})$

Since no 4-nitrophenyl 4-chlorobenzoate is found in the reaction of 4-chloro-4'-nitro-N-nitrosobenzanilide, the displaced bromide or nitrite ion presumably prefers not to attack the diazonium cation.

Such nucleophilic displacement by a benzoate ion in monohalogeno compounds is in contrast to Suschitzky's observations[72,73] that halogens other than fluorine are not displaced by a benzoate ion.

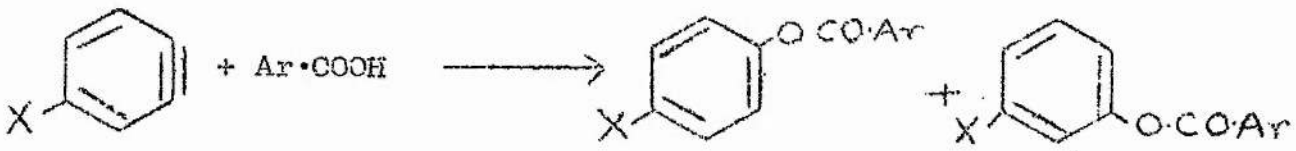
There are therefore two possible reactions leading to ester formation:

$$X\cdot C_6H_4N_2^+ + ArCO_2^- \xrightarrow{(a)} X\cdot C_6H_4\cdot O\cdot COAr + N_2$$

$$X\cdot C_6H_4N_2^+ + ArCO_2^- \xrightarrow{(b)} Ar\cdot CO\cdot O\cdot C_6H_4N_2^+ + X^- \longrightarrow Ar\cdot CO\cdot O\cdot C_6H_4Cl$$

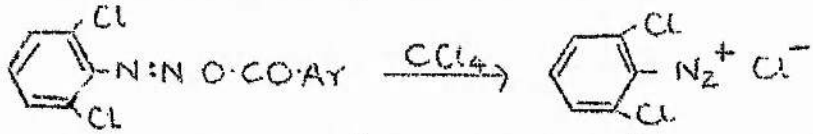
Path (a) will be operative alone, unless the substituent X is a good leaving group.

It must be noted that there is an absence of isomeric esters in those reactions, in contrast to the reaction of o-t-butyl-N-nitroso-acetanilide in benzene,[80] which suggests the absence of any true aryne intermediate. The usual, established reaction between an aryne and a carboxylic acid is as follows:[117]



5. Formation of Acyl Halides.

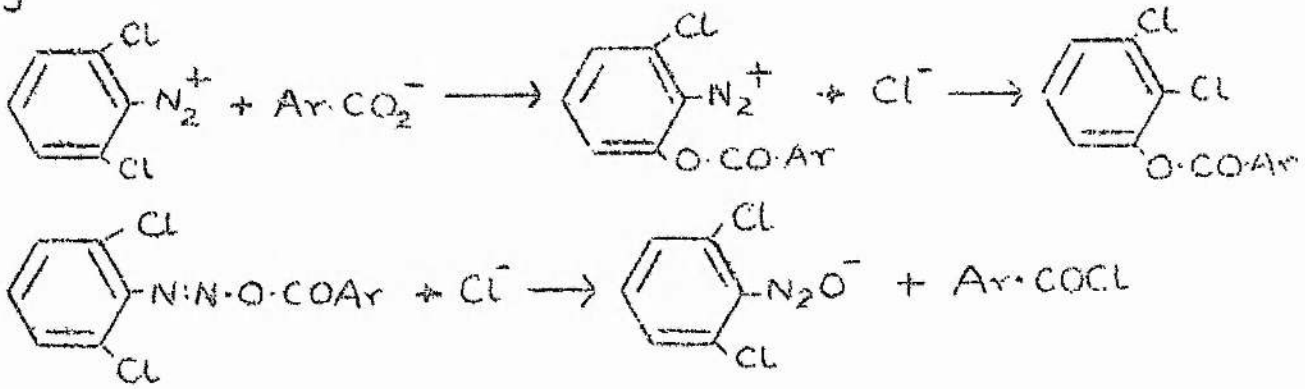
The main product in the reaction of 2',4,6'-trichloro-N-nitroso-benzanilide is p-chlorobenzoyl chloride (45%) [see Table 9, p. 85]. This may have arisen directly from the diazonium chloride, as shown:



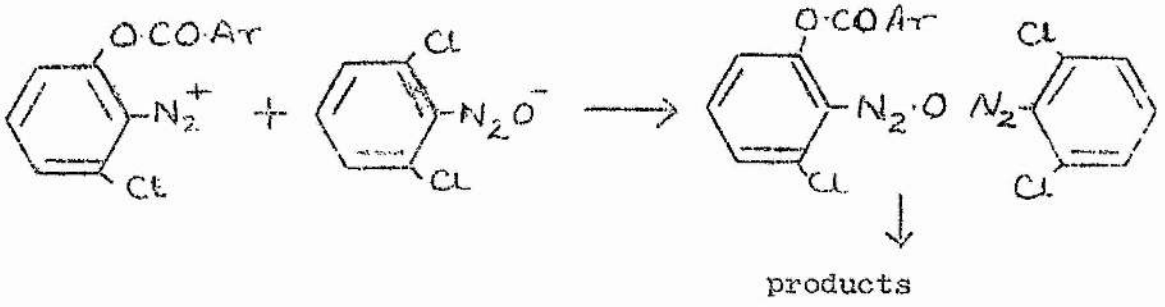
$$Ar'\cdot N{:}N\cdot O\cdot COAr + Cl^- \longrightarrow Ar'\cdot N_2O^- + Ar\cdot COCl$$

However, since the acid chloride is the main product of the reaction of this nitrosoamide with benzene, and since acid chlorides are not formed to any great extent in any other reaction, it is more probable that the chloride ion is produced by nucleophilic substitution. Such a reaction would be similar to that proposed by Suschitzky[72,73] to explain the production of acyl fluorides from reactions of p-fluoro-N-nitrosoacylarylamines with benzene.

e.g.



possibly



This reaction scheme has already been proposed to account for the presence of 2,3-dichlorophenyl 4-chlorobenzoate [25, p.139] in this reaction.

A third possibility, again unlikely because it would be expected to occur in every reaction, is the following sequence of reactions:

$$Ph\cdot N{:}N\cdot O\cdot CO\cdot Ar \longrightarrow PhN_2^{+} + ArCO_2^{-}$$

$$PhN_2^{+} \longrightarrow Ph^{+} \xrightarrow{CCl_4} PhCl + \overset{+}{C}Cl_3$$

$$ArCO_2^{-} + \overset{+}{C}Cl_3 \longrightarrow Ar\cdot CO\cdot O\cdot CCl_3 \longrightarrow Ar\cdot COCl + COCl_2$$

6. Miscellaneous Products.

Some further products of the reaction of 4'-bromo-4-chloro-N-nitrosobenzanilide [p-Br·$C_6H_4$N(NO)·CO·Ar] require an explanation. Hydrogen chloride is apparently produced in the reaction, since the addition of aniline to distillation fractions results in the production of aniline hydrochloride. This may have arisen by abstraction of hydrogen from the nitrosoamide by a chloride ion.

The brown colour which developed in the carbon tetrachloride distillates after a few days, but which was discharged by the addition of cyclohexene, is probably due to bromine, but there is no proof of this, the quantity of the addition product with cyclohexene being too small to be detected.

Unidentified solids obtained from the reactions of 4'-bromo-4-chloro-N-nitrosobenzanilide [p-Br·$C_6H_4$N(NO)·CO·$C_6H_4$Cl (-p)] and 4,4'-dibromo-N-nitrosobenzanilide [p-Br·$C_6H_4$·N(NO)·CO·$C_6H_4$·Br (-p)] seem to be identical from the I.R. spectrum, and from m.p. and mixed

m.p. (181°). These compounds must thus arise from the p-Br·$C_6H_4$·N- moiety. The I.R. spectrum shows >NH and >C=O absorption. The possibility of its being N·N'-bis-(4-bromophenyl)-urea [p·Br·$C_6H_4$·NH·CO·NH·$C_6H_4$·Br(p)] can be ruled out by its m.p. (lit. 330°) and analysis [Found: C, 44.2; H, 2.5; N, 7.9%. $C_{13}H_{10}Br_2N_2O$ requires C, 42.2; H, 2.7; N, 7.6%].

Further, the reaction of 2'-bromo-4-chloro-N-nitrosobenzanilide in carbon tetrachloride gives a solid m.p. 228° [Found: C, 44.0; H, 2.4; N, 7.9%] which appears to be isomeric with the previous compounds on the basis of the analysis and the I.R. spectra. Sodium fusion of this solid shows the presence of bromine and nitrogen. These compounds are as yet unidentified.

7. Summary of Reactions of N-Nitrosoacylarylamines with Benzene and Carbon Tetrachloride.

The products of the reaction of N-nitrosoacylarylamines in benzene have been explained in the preceeding pages (pp. 130-136) using a modification of the scheme proposed by Rüchardt et al.

In the reaction of N-nitrosoacylarylamines in carbon tetrachloride the accountance of the products is much lower than in benzene, often less than 50% . Much intractable residue is formed. This is found to contain nitrogen and chlorine, butgives no reaction on attempted reduction or hydrolysis with acid and alkali. It therefore does not contain -N=N- or R·O·$\overset{O}{\overset{\|}{C}}$ - linkages. Apart from the unidentified products in reactions of compounds containing a bromo substitutent (see p.154), explanations have been given for the presence of all

products except the carboxylic acid, which in most cases is the major product.

A typical reaction scheme is shown below.

$$Ar{\cdot}N(NO){\cdot}CO{\cdot}Ar' \longrightarrow Ar{\cdot}N{:}N{\cdot}O{\cdot}CO{\cdot}Ar' \rightleftharpoons Ar{\cdot}N_2^{+} + \bar{O}{\cdot}CO{\cdot}Ar'$$

$$Ar{\cdot}N{:}N{\cdot}O{\cdot}CO{\cdot}Ar' + \bar{O}{\cdot}CO{\cdot}Ar' \longrightarrow Ar{\cdot}N_2O^{-} + (Ar'CO)_2O$$

$$Ar{\cdot}N_2^{+} + \bar{O}{\cdot}CO{\cdot}Ar' \longrightarrow Ar{\cdot}O{\cdot}CO{\cdot}Ar' + N_2$$

$$Ar{\cdot}N_2^{+} + Ar{\cdot}N_2O^{-} \longrightarrow Ar{\cdot}N_2{\cdot}O{\cdot}N_2{\cdot}Ar \longrightarrow Ar{\cdot} + N_2 + Ar{\cdot}N_2O{\cdot}$$

$$Ar{\cdot}N_2^{+} \longrightarrow Ar^{+} \xrightarrow{CCl_4} ArCl + \overset{+}{C}Cl_3$$

$$Ar{\cdot} + CCl_4 \longrightarrow ArCl + {\cdot}CCl_3$$

$$Ar{\cdot}N_2O{\cdot} + {\cdot}CCl_3 \longrightarrow Ar{\cdot}N_2{\cdot}O{\cdot}CCl_3 \longrightarrow Ar{\cdot}N_2^{+}\ Cl^{-} + COCl_2$$

$$Ar{\cdot}N_2O^{-} + \overset{+}{C}Cl_3 \longrightarrow Ar{\cdot}N_2{\cdot}O{\cdot}CCl_3 \longrightarrow Ar{\cdot}N_2^{+}\ Cl^{-} + COCl_2$$

$$Ar{\cdot}N_2^{+}\ Cl^{-} \longrightarrow ArCl\ (+\text{ exchange products}) + N_2$$

This scheme, however, cannot accommodate the formation of carboxylic acid (Ar'COOH). It has been suggested (p. 140 ) that the o-position in the nitrosoamide provides the acidic hydrogen, possibly via an aryne intermediate. Results of experiments designed to trap any intermediate arynes will now be discussed.

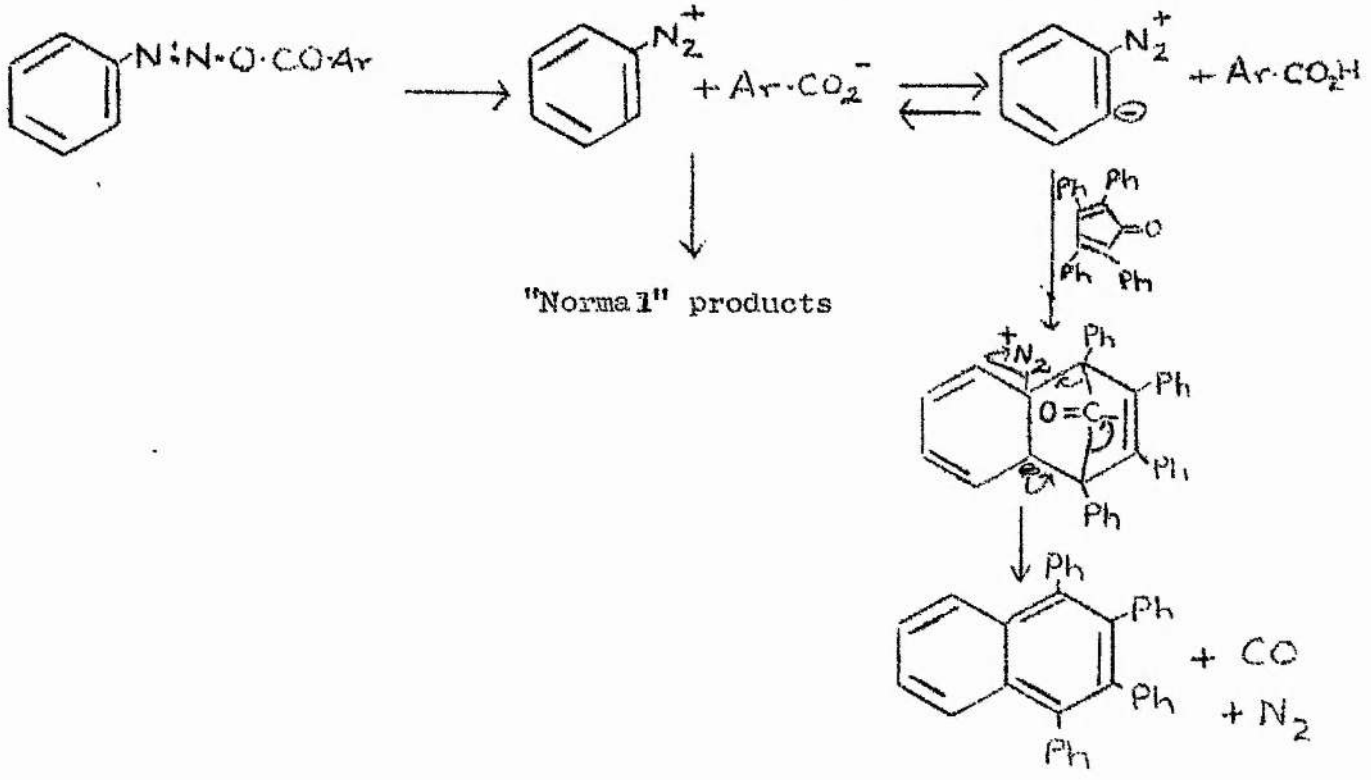
Decomposition of N-Nitrosoacylarylamines in Benzene and in Carbon Tetrachloride in the Presence of Dienes as Aryne Traps.

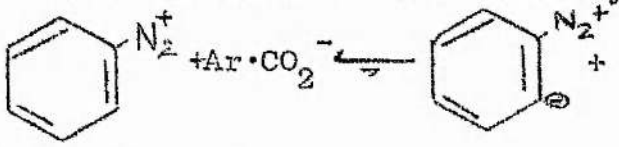
In an attempt to trap aryne intermediates in reactions of nitrosoacylarylamines without bulky o-substituents, reactions have been carried out in the presence of known aryne traps. No benzyne/furan adducts have been isolated from reactions of 4-chloro-N-nitrosobenzanilide or 4-chloro-4'-methyl-N-nitrosobenzanilide in the presence of furan, although p-chlorobenzoic acid is isolated in high yield, and control experiments have shown that the adduct is stable under the reaction conditions. In the presence of anthracene, no triptycene is obtained from the reaction of N-nitrosoacetanilide, but triptycene (4%) is isolated from the reaction of 4-chloro-N-nitrosobenzanilide. The use of the more reactive diene, 2,3,4,5-tetraphenylcyclopentadienone, however, has led to the isolation of 1,2,3,4-tetraphenylnaphthalene (23% and 37% respectively) from reactions of N-nitrosoacetanilide and 4-chloro-N-nitrosobenzanilide.

When authentic benzyne is generated from amyl nitrite and anthranilic acid in the presence of mixtures of 2,3,4,5-tetraphenylcyclopentadienone and anthracene and of 2,3,4,5-tetraphenylcyclopentadienone and furan,[153] 1,2,3,4-tetraphenylnaphthalene alone is isolated from the reactions, showing that 2,3,4,5-tetraphenylcyclopentadienone is superior to both anthracene and furan as a benzyne trap. However, when N-nitrosoacetanilide is allowed to decompose in benzene in the presence of 2,3,4,5-tetraphenylcyclopentadienone and furan, no benzyne addition products are obtained, and the major product is 2-phenylfuran.[153] It appears, therefore, that the intermediate being trapped by

2,3,4,5-tetraphenylcyclopentadienone in reactions of N-nitrosoacylarylamines may not be true benzyne. Phenyl radicals are, however, not responsible for the formation of 1,2,3,4-tetraphenylnaphthalene, since this is not obtained when benzoyl peroxide or phenylazotriphenylmethane is allowed to decompose in the presence of 2,3,4,5-tetraphenylcyclopentadienone.[153]

Since the above results indicate that the intermediate being trapped by these dienes is neither true benzyne nor an aryl radical, it is possible that it is dipolar in nature, and so will react only with the more reactive, polarisable dienes, such as 2,3,4,5-tetraphenylcyclopentadienone. This is supported by the fact that N-nitrosoacetanilide has been reported[153] to yield an adduct with 1,3-diphenylisobenzofuran as trap. In the absence of such dienes, this dipolar intermediate would be unobserved, and would decompose to give the "normal" reaction products. The formation of this intermediate, and the reaction with dienes, may be as follows:



In the presence of water, the formation of 1,2,3,4-tetraphenylnaphthalene in the reaction of 4-chloro-N-nitroso-benzanilide with carbon tetrachloride and 2,3,4,5-tetraphenylcyclo-pentadienone is inhibited, and the products of the reaction become those of a similar reaction without the diene present. This effect can be explained on the reaction scheme overleaf. The water would compete with the diazonium cation as the donor of the acidic hydrogen i.e. the equilibrium would be  Also if the dipolar intermediate does form, it will readily remove a proton from water giving the diazonium cation. The equilibrium will therefore lie well over to the left and very little 1,2,3,4-tetraphenyl-naphthalene will be produced, although the normal products will be obtained.

If the above scheme is correct, i.e. removal of the o-hydrogen by the benzoate ion to produce the intermediate which reacts with dienes, then the nature of the substituent in Ar should influence the yield of the addition product. Reactions, under similar conditions, carried out using compounds of the structure $Ph\cdot N(NO)\cdot CO\cdot Ar$, with Ar = $-CH_3$, $-C_6H_4Cl(-p)$, $C_6H_4NO_2(-p)$, $-C_6H_4Me(p)$, and using 2,3,4,5-tetraphenylcyclopentadienone, indicate that this is the case. The yield of 1,2,3,4-tetraphenyl-naphthalene is found to be in the following decreasing order:

$p\text{-}Cl\cdot C_6H_4-$, 37% > $p\cdot MeC_6H_4$, 29% > $-CH_3$, 21% > $p\cdot NO_2\cdot C_6H_4-$, 14%

The dissociation constants for the corresponding acids ($Ar\cdot COOH$) are in the order:

$p\text{-}NO_2\cdot C_6H_4- > p\text{-}Cl\cdot C_6H_4- > p\text{-}Me\cdot C_6H_4- > CH_3-$

The weakest acid will have the most nucleophilic anion and might therefore be expected to remove hydrogen from the ring most readily, in which case the yields of 1,2,3,4-tetraphenylnaphthalene expected would be in the order:

$$-CH_3 > \underline{p}\text{-}Me\cdot C_6H_4- > \underline{p}\text{-}Cl\cdot C_6H_4-, > \underline{p}\text{-}NO_2\cdot C_6H_4-$$

As predicted by this scale, the compound with the p-nitro substituent does give the lowest yield of 1,2,3,4-tetraphenylnaphthalene. However, the yields from the other nitrosoamides do not correspond to those predicted. It may be that intermediate equilibria in the reactions upset the scale. The results, although not conclusive, suggest that the basic strength of the anion $Ar\cdot CO_2^-$ does exert some influence on the formation of the addition product.

The results of experiments using substituted N-nitrosobenzanilides $[R\cdot C_6H_4\cdot N(NO)\cdot CO\cdot C_6H_4Cl(\underline{p})]$ in both benzene and carbon tetrachloride in the presence of the diene show that the nature of the solvent has little influence on the yield of the substituted 1,2,3,4-tetraphenylnaphthalene. (See Table 16).

Table 16.

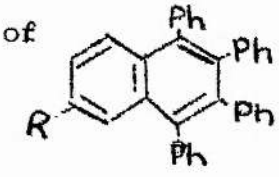
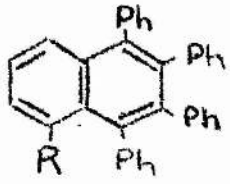
Yield (%) of Substituted 1,2,3,4-Tetraphenylnaphthalenes from Reactions in Benzene and Carbon Tetrachloride.

| R in $R \cdot C_6H_4 \cdot N(NO) \cdot CO \cdot C_6H_4Cl(p)$ | H | o-Br | m-Br |
|---|---|---|---|
| Yield (%) in Benzene | 37 | 0 | 73 |
| Yield (%) in Carbon Tetrachloride | 37 | 0 | 70 |

The results, however, do show the influence of the substituent R on the yield of addition product. These results are detailed in Tables 11 and 12 but are summarised below for convenience (Table 17).

Table 17

Yield (%) of Product from Reactions of Substituted Nitrosoamides with Carbon Tetrachloride and 2,3,4,5-Tetraphenylcyclopentadienone.

| R in $RC_6H_4N(NO)CO \cdot C_6H_4 \cdot Cl(p)$ | H | o-Br | m-Br | m-Me | $m\text{-}NO_2$ | p-Br | p-Me | $p\text{-}NO_2$ |
|---|---|---|---|---|---|---|---|---|
| Yield (%) of  | 37 | 0 | 0 | 12 | 0 | 4 | 1 | 0 |
| Yield (%) of  | | 0 | 70 | 21 | 63 | 0 | 0 | 0 |

o-Substituted Nitrosoamides

From tables 16 and 17 it can be seen that the reactions of nitrosoamides with a substituent in the o-position in the amino moiety give no substituted 1,2,3,4-tetraphenylnaphthalenes. The yields of other products from these reactions in the presence of 2,3,4,5-tetraphenylcyclopentadienone show only a slight variation from those of similar reactions in the absence of the diene. These results are summarised in Table 18.

Table 18

Yields (%) of Products from Reactions of 2'-Bromo-4-Chloro-N-Nitrosobenzanilide in Benzene and Carbon Tetrachloride in the Presence and Absence of 2,3,4,5-Tetraphenylcyclopentadienone. [Ar·N(NO)·CO·Ar']

| | Ar'COOH | | $(Ar'CO)_2O$ | | ArCl | | Ar'CO·O·Ar | | Adduct | | Ar·Ph | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | No Trap | Trap | No Trap | Trap | No Trap | Trap | No Trap | Trap | No Trap | Trap | No Trap | Trap |
| Reactions in $CCl_4$ | 29 | 24 | 17 | 22 | 38 | 23 | 1 | 0 | 0 | 0 | | |
| Reactions in PhH | 80 | 69 | 0 | 0 | - | - | 0 | 0 | 0 | 0 | 68 | 21 |

It can be seen that the yield of p-chlorobenzoic acid falls slightly in reactions in both benzene and carbon tetrachloride on the addition of the diene. There is, however, a significant drop in the yield of

2-bromobiphenyl from the reaction in benzene on the addition of the aryne trap, and also a reduction in the yield of aryl chloride in the reaction with carbon tetrachloride. It would appear that, in the presence of the diene, no addition product is formed, but some part of the reaction is suppressed.

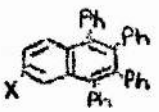
p-Substituted Nitrosoamides.

In the reactions of p-Substituted N-nitrosobenzanilides [e.g. p·Br·$C_6H_4$N(NO)·CO·Ar·] in carbon tetrachloride in the presence of 2,3,4,5-tetraphenylcyclopentadienone, very low yields (0-4%) of the substituted 1,2,3,4-tetraphenylnaphthalenes are obtained (see Table 17, p.131). The yields of the other products of the reaction show significant variation from those produced in similar reactions in the absence of the diene, and they are compared in Table 19.

Table 19

Yield (%) of Products from Reactions of p-Substituted N-Nitrosobenzanilides in Carbon Tetrachloride in the Presence and Absence of 2,3,4,5-Tetraphenyl cyclopentadienone.

(Ar' = p·Cl·$C_6H_4$)

| Ar in ArN(NO)·CO·Ar' | Ar'COOH | | $(ArCO)_2O$ | | ArCl | | Ar'COOAr | | Ar'COOAr' | |  |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | No Trap | Trap | No Trap | Trap | No Trap | Trap | No Trap | Trap | No Trap | Trap | Trap |
| p·Me·$C_6H_4$- | 74 | 63 | 6 | 11 | 25 | 23 | 0.5 | 0 | 0 | 0 | 1 |
| p·$NO_2$·$C_6H_4$- | 49 | 18 | 19 | 23 | 56 | 18 | 0.8 | 0 | 6 | <1 | 4 |
| p·$NO_2$·$C_6H_4$- | 68 | 4 | 9 | 18 | 34 | 10 | 0 | 0 | 11 | 9 | 0 |

It can be seen from Table 19 that the most significant variation occurs in the amount of p-chlorobenzoic acid formed in the presence and absence of the diene. In all cases, the yield of acid is reduced by the addition of the diene, but this reduction is exceptionally large in the case of 4-nitro-4'-chloro-N-nitrosobenzanilide, where almost no acid is formed in the presence of the diene, although a high yield is produced in reactions without trap. There is a similar, though less severe, reduction in the yields of aryl halides, and displacement of the substituent by chlorine is still apparent to a slight extent in the reaction of 4'-bromo-4-chloro-N-nitrosobenzanilide although it is absent in the reaction of 4-chloro-4'-nitro-N-nitrosobenzanilide. In contrast, the yields of p-chlorobenzoic anhydride show an increase in all reactions in the presence of the diene, and the anhydride is the major product identified in the reaction of 4-chloro-4'-nitro-N-nitrosobenzanilide. The yields of substituted 1,2,3,4-tetraphenyl-[illegible] naphthalenes are very low.

In contrast to the reaction in the absence of the diene, no phosgene is produced and no brown colour develops in the carbon tetrachloride solution in the reaction of 4'-bromo-4-chloro-N-nitrosobenzanilide in the presence of the diene. A considerable quantity of brown material is produced from the reaction in the presence of the diene.

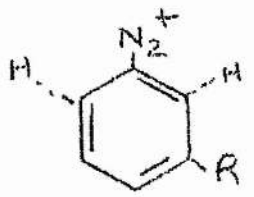
The reaction of 4-chloro-4'-nitro-N-nitrosobenzanilide with carbon tetrachloride and 2,3,4,5-tetraphenylcyclopentadienone produces

a compound, m.p. 167-168° [Found: C, 88.0; H, 4.9%. M.Wt. 400] which contains neither nitrogen nor chlorine. The I.R. spectrum is similar to that of 2,3,4,5-tetraphenylcyclopentadienone, showing carbonyl absorption at 1720 $cm.^{-1}$ This compound is still unidentified.

It is obvious that p-substituted nitrosoamides react with 2,3,4,5-tetraphenylcyclopentadienone in such a way that the normal reaction is suppressed. This is least noticeable when the substituent is a methyl group, and most noticeable when a nitro group is present, and leads to a decrease in yield of all products except the anhydride. The identity of the above by-products must be established before the complete reaction can be formulated.

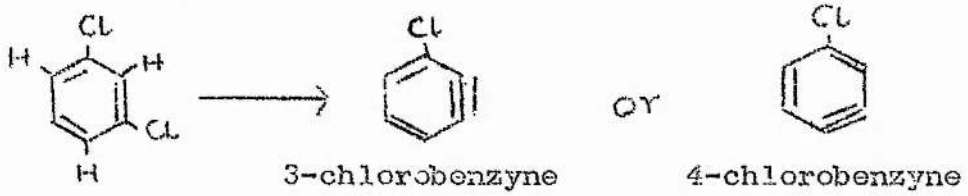
Unsubstituted and m-Substituted Nitrosoamides.

The reactions of unsubstituted and m-substituted nitrosoamides [e.g. m-$Br \cdot C_6H_4N(NO) \cdot CO \cdot Ar$] in both benzene and carbon tetrachloride in the presence of 2,3,4,5-tetraphenylcyclopentadienone give high yields of addition products (33-70%) [See Table 17, p. 131]. In the reaction of 4-chloro-3'-methyl-N-nitrosobenzanilide two addition products can be detected by N.M.R. (see p. 104), while only one product is present in each of the other reactions (see pp.102,105). This suggests that, for formation of appreciable amounts of an addition product with a diene, a substituent must be present in the m-position in the amino moiety of the molecule, i.e. o- or p- to the hydrogen which is being removed in the formation of the acid

i.e. 

Also, the inductive effect of the substituent appears to influence the yields of addition product formed in the reactions of m-substituted nitrosoamides with the diene (m-Br > m-$NO_2$ >>H > m-Me). Both -$NO_2$ and -Br have a strong -I effect, which would be evident to a very much greater extent in the position o- to these substituents than in the p-position. Thus one hydrogen only (the o-hydrogen) would be removed, and so only one addition product would be formed. The methyl substituent, on the other hand, has a +I effect, and there will thus not be a strong directing influence to the o-hydrogen. Both o- and p-hydrogens could thus be removed, giving a mixture of addition products with the diene.

A similar effect has been recorded[154] in the reaction of m-dichlorobenzene with potassamide in liquid ammonia. In this case, there are two arynes possible:



3-chlorobenzyne or 4-chlorobenzyne

It has been found that reaction proceeds largely via the 3-chlorobenzyne (97%) and only very slightly via the 4-chlorobenzyne (3%). The enhanced acidity of the hydrogen o- to both chlorine atoms as opposed to those o- to only one chlorine atom and p- to the other

Table 20

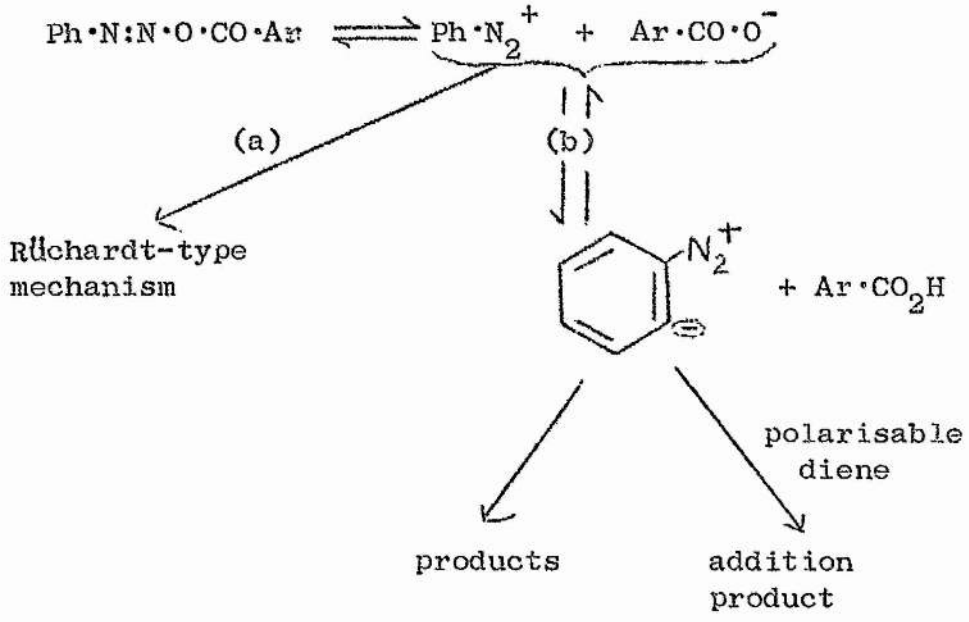
| | Ar in Ar·N(NO)·CO·Ar' (Ar'=p·Cl·$C_6H_4$-) | Ar'·COOH | | $(Ar'CO)_2O$ | | Ar·Cl | | Ar'·CO·O·Ar | | Ar·Ph | | "Adduct" |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | No Trap | Trap | No Trap | Trap | No Trap | Trap | No Trap | Trap | No Trap | Trap | Trap |
| Reactions in $CCl_4$ | Ph | 46 | 49 | 15 | 0 | 27 | 4 | 18 | 0 | 0 | 0 | 37 |
| | m-Me·$C_6H_4$- | - | 71 | - | 0 | - | 5 | - | 0 | 0 | 0 | 33 |
| | m-Br·$C_6H_4$- | 57 | 32 | 13 | 0 | 36 | 2 | 0.2 | 0 | 0 | 0 | 70 |
| | m-$NO_2$·$C_6H_4$- | - | 84 | - | 0 | - | 0 | - | 0 | 0 | 0 | 63 |
| Reactions in PhH | Ph | 33 | 79 | 0 | 0 | 0 | 0 | 1.0 | 0.5 | 33 | 4 | 37 |
| | m-Br·$C_6H_4$- | 92 | 37 | 0 | 0 | 0 | 0 | 0 | 0 | 62 | 1 | 73 |
| | Ar' in Ar·N(NO)·CO·Ar' (Ar = Ph) | | | | | | | | | | | |
| Reactions in $CCl_4$ | $-CH_3$ | 54 | - | 15 | - | 33 | 1 | 5 | 0 | 0 | 0 | 21 |
| | $-C_6H_4$·Me(p) | - | 52 | - | 0 | - | 0 | - | 10 | 0 | 0 | 29 |
| | $-C_6H_4$·$NO_2$(p) | - | 44 | - | 0 | - | 16 | - | 10 | 0 | 0 | 14 |

is said to account for this effect.

In such reactions, where high yields of 1,2,3,4-tetraphenylnaphthalenes are obtained [e.g. with m-Br·$C_6H_4$·N(NO)·CO·$C_6H_4$Cl(p)], p-chlorobenzoic acid is the only other major product isolated. The results of reactions of unsubstituted and m-substituted nitrosoamides in benzene and in carbon tetrachloride in the presence and absence of 2,3,4,5-tetraphenylcyclopentadienone are summarised in Table 20.

p-Chlorobenzoic anhydride is no longer among the products of the reactions, and the yields of aryl halides and esters have decreased considerably in the presence of the diene in carbon tetrachloride. A similar reduction in the yield of biphenyl is produced in benzene on the addition of the diene.

Since a high yield of tetraphenylnaphthalene is associated with a reduction in the yield of aryl halide, these compounds appear to have a common precursor, which cannot be an aryl radical itself, since aryl radicals have been shown[153] to produce no 1,2,3,4-tetraphenylnaphthalene with the diene. A typical scheme may, however, be as follows:



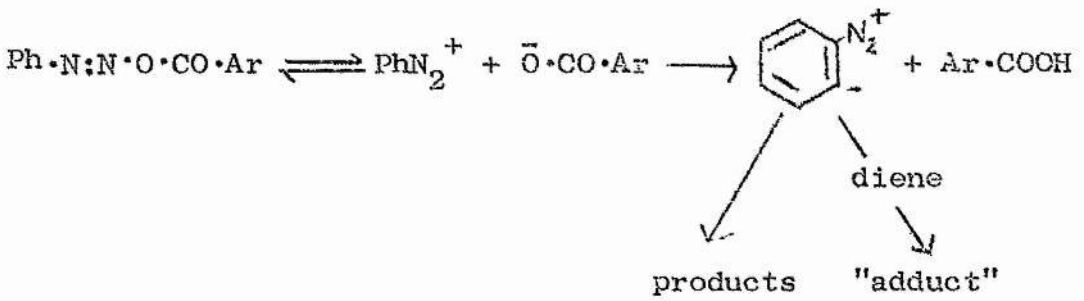

In the presence of a polarisable diene, the dipolar intermediate would be detected; its removal would cause the whole reaction to proceed by path (b), and no other products would be obtained. In the absence of this diene, the reaction would proceed via paths (a) and (b), the dipolar intermediate reacting to give either identifiable products or tars. However, the anomalous reactions of p-substituted nitrosoamides (i.e. the apparent suppression of the whole reaction apart from formation of the acid anhydride) especially the reaction of p-$NO_2$·$C_6H_4$·N(NO)·CO·$C_6H_4$Cl(p), cannot be explained by this scheme. Nor does it explain why high yields of addition products are not formed in reactions of compounds with substituents in positions other than the m-position, even although high yields of acid may be produced in these cases in carbon tetrachloride.

## CONCLUSION

In conclusion, it can be said that the decompositions of N-nitrosoacetanilides and N-nitrosobenzanilides appear to follow the same reaction mechanism in the same solvent. From the E.S.R. spectra it would appear that different mechanisms operate in benzene and carbon tetrachloride, but, since the pattern of behaviour in both of these solvents on the addition of 2,3,4,5-tetraphenylcyclopentadienone is identical, there must be at least one step in the reaction common to both solvents. Neither the mechanism proposed by Rüchardt nor that proposed by Perkins explains this reaction with an aryne trap, although the reaction in benzene in the absence of the diene can be adequately explained.

It has previously been shown that the reaction in benzene is radical in nature, but there is no conclusive evidence to indicate that the reaction in carbon tetrachloride is also a radical process. Although the E.S.R. spectrum shows the presence of an unknown radical in minute concentration, the absence of hexachloroethane in the products suggests the absence of trichloromethyl radicals. It is obvious from the results that the intermediate reacting with the diene is neither true benzyne nor an aryl radical, and it could be dipolar in nature.

If Rüchardt's scheme is operative at all, it must be modified to account for the reaction with the diene. A possible modification for the reaction scheme in benzene is shown overleaf:




$$Ph\cdot N{:}N\cdot O\cdot CO\cdot Ar + \bar{O}\cdot CO\cdot Ar \longrightarrow Ph\cdot N_2O^- + (Ar\cdot CO)_2O$$

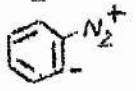
$$Ph\cdot N_2^+ + Ph\cdot N_2O^- \longrightarrow Ph\cdot N_2\cdot O\cdot N_2\cdot Ph \longrightarrow Ph\cdot + N_2 + Ph\cdot N_2O\cdot$$

$$Ph\cdot + PhH \longrightarrow \sigma\text{-complex} \xrightarrow{Ph\cdot N_2O\cdot} Ph\cdot Ph + Ph\cdot N_2\cdot OH$$

$$Ph\cdot N_2\cdot OH + Ar\cdot CO\cdot O^- \longrightarrow Ph\cdot N_2O^- + ArCO_2H$$

The reaction in carbon tetrachloride, however, cannot yield p-chlorobenzoic acid according to this scheme. Also, any scheme must incorporate the formation of a diazonium chloride. The E.S.R. spectrum of the reaction in carbon tetrachloride does not support the presence of the phenyl diazotate radical, $Ph\cdot N_2O\cdot$. Further, it has been shown (see p. 134) that the absence of 2,6-dichlorobiphenyl from the reaction of 2,4,6'-trichloro-N-nitrosobenzanilide in benzene seems to suggest the absence of a diazoanhydride. A reaction scheme based on ions and not radicals can explain the products.

$$Ph{\cdot}N{:}N{\cdot}O{\cdot}CO{\cdot}Ar \longrightarrow Ph{\cdot}N_2^{+} + Ar{\cdot}CO_2^{-}$$

$$Ph{\cdot}N_2^{+} + Ar{\cdot}CO_2^{-} \longrightarrow Ar{\cdot}COOH + \text{  }$$

diene

products "adduct"

$$Ph{\cdot}N_2^{+} \longrightarrow Ph^{+} + N_2 \xrightarrow{CCl_4} PhCl + \overset{+}{C}Cl_3$$

$$Ar{\cdot}CO_2^{-} + Ph{\cdot}N{:}N{\cdot}O{\cdot}CO{\cdot}Ar \longrightarrow (Ar{\cdot}CO)_2O + Ph{\cdot}N_2O^{-}$$

$$Ph{\cdot}N_2O^{-} + \overset{+}{C}Cl_3 \longrightarrow Ph{\cdot}N_2{\cdot}O{\cdot}CCl_3 \longrightarrow Ph{\cdot}N_2^{+}\ Cl^{-} + COCl_2$$

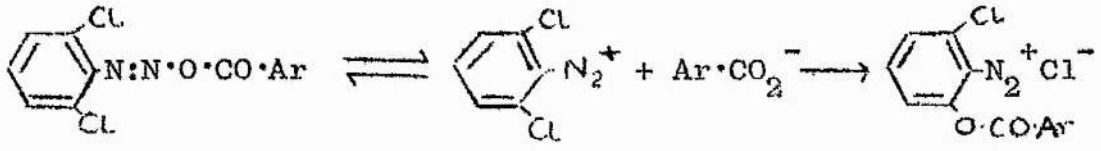
$$Ph{\cdot}N_2^{+} + CCl_4 \longrightarrow Ph{\cdot}N_2^{+}\ Cl^{-} + \overset{+}{C}Cl_3$$

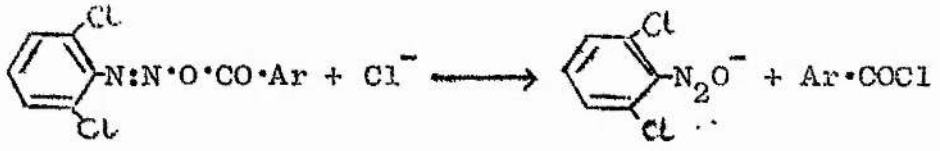
$$Ph{\cdot}N_2^{+}\ Cl^{-} \longrightarrow PhCl + N_2$$

$$Ph{\cdot}N_2^{+} + O^{-}CO{\cdot}Ar \longrightarrow Ar{\cdot}CO{\cdot}O{\cdot}Ph + N_2$$

Radical intermediates cannot be ignored completely because an E.S.R. signal is obtained, although it is very weak. Perhaps radical and ionic mechanisms operate together in both benzene and in carbon tetrachloride.

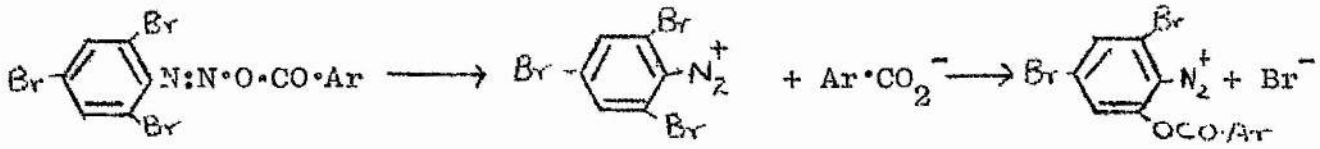
The reactions of nitrosoamides having both o-positions in the amino moiety substituted [e.g. 2',4,6'-trichloro-N-nitrosobenzanilide] cannot yield a dipolar intermediate, and so p-chlorobenzoic acid is not produced from reactions in benzene or in carbon tetrachloride. In this case, one of the o-substituents is displaced by a benzoate ion

e.g. 



Each cation and anion may then react according to the scheme already proposed above or by that on p.142.

A similar reaction takes place with 4-chloro-2',4',6'-tribromo-N-nitrosobenzanilide, as shown:



The reaction scheme (p.171)would then operate, together with those already proposed (pp. 142-152) to yield aryl halides and esters.

These schemes will not, however, explain why, in some reactions in the presence of 2,3,4,5-tetraphenylcyclopentadienone, there is formed a high yield of acid, but no benzyne-type adduct [e.g. in the reaction of p-Me·$C_6H_4$·N·(NO)·CO·$C_6H_4$·Cl(p)] or why there is an apparent suppression of the normal reaction in the case of p-$NO_2$·$C_6H_4$·N·(NO)·CO·$C_6H_4$·Cl(p).

Further work will be necessary to establish whether or not there are radicals present in reactions in carbon tetrachloride. It will also be important to ascertain that only the o-hydrogen atom is removed in the formation of the acid. This could be done by replacement of the o-hydrogens by deuterium, and will enable the structure of the reactive intermediate to the known with more certainty. A vital clue to the reaction of p-substituted nitrosoamides with 2,3,4,5-tetraphenylcyclopentadienone may come from the identification of the compound formed in the reaction of p-$NO_2$·$C_6H_4$·N(NO)·CO·$C_6H_4$·Cl(p) with this diene. A high yield of brown tars and glasses is formed in every reaction. Perhaps the clue to the structure of the intermediate will be found if the nature of these products can be ascertained.

## REFERENCES


1 W.S.M. Grieve and D.H. Hey, J. Chem. Soc., 1934, 1797.

2 C. Rüchardt and E. Merz, Tetrahedron Letters, 1964, 2431.

3 W.A. Waters, J. Chem. Soc., 1939, 864.

4 C.E. Waring and J.R. Abrams, J. Amer. Chem. Soc., 1941, 33, 2757.

5 M.R. Petitt and J.C. Tatlow, J. Chem. Soc., 1954, 1941.

6 E. Bamberger, Ber, 1895, 28, 403; 1896, 29, 446.

7 J. Elks and D.H. Hey, J. Chem. Soc., 1943, 441.

8 J.I.G. Cadogan, D.A. Roy, and D.M. Smith, J. Chem. Soc., 1966(C), 1249; J.I.G. Cadogan, J. Chem. Soc., 1962, 4257.

9 D.H. Hey, J. Chem. Soc., 1934, 1966.

10 H. Wieland, K. Heyman, T. Tsatsas, D. Juchum, G. Varvoglis, G. Labriola, O. Dobblestein, and H.S. Boyd-Barrett, Annalen, 1934, 514, 145; M.G. Alder and J.E. Leffler, J. Amer. Chem. Soc., 1954, 76, 1425; R. Huisgen and H. Nakaten, Annalen, 1954, 586, 70.

11 S.G. Cohen and Chi Hua Wang, J. Amer. Chem. Soc., 1953, 75, 5504.

12 D.H. Hey, J. Chem. Soc., 1952, 1974.

13 D.R. Augood, D.H. Hey, and G.H. Williams, J. Chem. Soc., 1952, 2094; 1953, 44.

14 D.H. Hey, A. Nechvatal and T.S. Robinson, J. Chem. Soc., 1951, 2892.

15 D.H. Hey, M.J. Perkins, and G.H. Williams, J. Chem. Soc., 1963, 5604.

16 D.H. Hey, C.J.M. Stirling, and G.H. Williams, J. Chem. Soc., (a) 1954, 2747; (b) 1955, 3963; (c) 1956, 1475.

17 D. Bryce-Smith and P. Clarke, J. Chem. Soc., 1956, 2264.

18 B.M. Lynch and K.H. Pausacker, Austral. J. Chem., 1957, 10, 329; J.E. Leffler, W.J.M. Mitchell, and B.C. Meron, J. Org. Chem., 1966, 31, 1153.

19 J.M. Blair, D. Bryce-Smith, and B.W. Pengilly, J. Chem. Soc., 1959, 3174; G.A. Razuvaeu and Yu A Ol'dekep, J. Gen. Chem. (U.S.S.R.), 1949, 19, 711, 1485; 1951, 21, 1225.

20 D.H. Hey, D.A. Shingleton, and G.H. Williams, J. Chem. Soc., 1963, 5612.

21 W. Wolf and N. Kharasch, J. Org. Chem., 1965, 30, 2493; N. Kharasch and R.K. Sharma, Chem. Comm., 1966, 156.

22 De Los F. de Tar and R.A.J. Long, J. Amer. Chem. Soc., 1956, 80, 4742.

23 B.M. Lynch and K.H. Pausacker, Austral. J. Chem., 1957, 10, 165.

24 J.H. Waters, Diss. Abs., 1961, 22, 432.

25 C. Rüchardt and B. Freudenberg, Tetrahedron Letters, 1964, 3623.

26 H. Gelissen and P.H. Hermans, Ber., 1925, 58, 285, 476, 479, 764, 984, 2396; 1926, 59, 63, 662.

27 J. Boeseken and H. Gelissen, Rec. Trav. Chem., 1924, 43, 869.

28 W.S.M. Grieve and D.H. Hey, J. Chem. Soc., 1935, 689.

29 E.C. Butterworth and D.H. Hey, J. Chem. Soc., 1938, 116.

30 D.H. Hey and J. Peters, J. Chem. Soc., 1960, 79.

31 M.S. Kharasch, $H_4C_2$ McBay and N.H. Urry, J. Org. Chem., 1945, 10, 401.

32 W.A. Waters, J. Chem. Soc., 1937, 113, 2007; D.H. Hey, M.J. Perkins, and G.H. Williams, Tetrahedron Letters, 1963, 445.

33 J.I.G. Cadogan, D.H. Hey, and P.G. Hibbert, J. Chem. Soc., 1965 3939.

34 P.G. Hibbert, Ph.D. Thesis, London, 1963.

35 E. Fischer, Ber., 1876, 9, 464; 1877, 10, 959.

36 H. Pechmann and L. Frobenius, Ber., 1894, 27, 651.

37 E. Bamberger, Ber., 1894, 27, 914.

38 O. Kuhling, Ber., 1895, 28, 41.

39 O. Kuhling, Ber., 1896, 29, 165.

40 E. Bamberger, Ber., 1897, 30, 366.

41 H. Gelissen and P.H. Hermans, Ber., 1925, 58, 984.

42 H. Pechmann, Ber., 1898, 31, 2640.

43 M. Gomberg and W.E. Bachmann, J. Amer. Chem. Soc., 1924, 46, 2339; M. Gomberg and J.C. Pernert, J. Amer. Chem. Soc., 1926, 48, 1372; W.S.M. Grieve and D.H. Hey, J. Chem. Soc., 1938, 100.

44 W.A. Waters, J. Chem. Soc., 1938, 843, 1077; D.H. Hey and W.A. Waters, Chem. Rev., 1937, 21, 169.

45 A.T. Blomquist, J.R. Johnson, and H.J. Sykes, J. Amer. Chem. Soc., 1943, 65, 2446.

46 H.H. Hodgson, J. Chem. Soc., 1948, 348.

47 D.H. Hey and W.A. Waters, J. Chem. Soc., 1948, 882.

48 C.S. Rondestvedt and H.S. Blanchard, J. Amer. Chem. Soc., 1955, 77, 1769.

49 De Los. F. de Tar and H.J. Scheifele, J. Amer. Chem. Soc., 1951, 73, 1442.

50 H. France, I.M. Heilbron, and D.H. Hey, J. Chem. Soc., 1940, 372; J.W. Haworth, I.M. Heilbron, and D.H. Hey, J. Chem. Soc., 1940, 349, 1278; W.J. Adams, D.H. Hey, P. Mamalis, and R.E. Parker, J. Chem. Soc., 1949, 3181.

51 R. Huisgen and G. Horeld, Annalen, 1949, 562, 137.

52 R. Huisgen, Annalen, 1951, 573, 163.

53 De Los F. de Tar, J. Amer. Chem. Soc., 1951, 73, 1446.

54 R. Huisgen and L. Krause, Annalen, 1951, 574, 157.

55 D.H. Hey, J. Stuart-Webb, and G.H. Williams, J. Chem. Soc., 1952, 4657.

56 K. Heyns and W. von Bebenburg, Annalen, 1955, 595, 55.

57 R. Huisgen and H. Nakaten, Annalen, 1954, 586, 84.

58 R. Huisgen, Angew. Chem., 1950, 62, 369.

59 R. Huisgen, Annalen, 1951, 574, 184.

60 E. White, J. Amer. Chem. Soc., 1954, 76, 4497; 1955, 77, 6008.

61 E. White and C.A. Aufdermarsh, J. Amer. Chem. Soc., 1961, 83, 1174.

62 R. Huisgen and H. Reimlinger, Annalen, 1956, 599, 183.

63 F.G. Edwards and F.R. Mayo, J. Amer. Chem. Soc., 1950, 72, 1265.

64 R. Huisgen and H. Nakaten, Annalen, 1951, 573, 181.

65 C.G. Overberger and N.P. Marullo, J. Amer. Chem. Soc., 1961, 83, 1379.

66 E.L. Eliel, M. Eberhardt, O. Simamura, and S. Meyerson, Tetrahedron Letters, 1962, 749.

67 E.L. Eliel, Rev. Soc. Quim. Mex., 1963, 7(6), 229.

68 E.L. Eliel, J.G. Saha, and S. Meyerson, J. Org. Chem., 1965, 30, 2451.

69 E.L. Eliel and J.G. Saha, J. Amer. Chem. Soc., 1964, 86, 3581.

70 D.B. Denny, N.E. Gersham, and A. Appelbaum, J. Amer. Chem. Soc., 1964, 86, 3180.

71 E. Pfeil and O. Weissel, Ber., 1958, 91, 1170.

72 I.K. Barben and H. Suschitzky, J. Chem. Soc., 1960,2735.

73 P.Miles and H. Suschitzky, Tetrahedron, 1962, 18, 1369.

74 P.Miles and H. Suschitzky, Tetrahedron, 1963, 19, 385.

75 G. Binsch and C. Rüchardt, J. Amer. Chem. Soc., 1966, 88, 137.

76 G. Binsch, E. Merz, and C. Rüchardt, Ber., 1967, 100, 247.

77 G.R. Chalfont, D.H. Hey, K.S. Y. Liang, and M.J. Perkins, Chem. Comm., 1967, 367.

78 G.R. Chalfont and M.J. Perkins, J. Amer. Chem. Soc., 1967, 89, 3054.

79 J.I.G. Cadogan, D.H. Hey, and G.H. Williams, J. Chem. Soc., 1954, 3352.

80 J.I.G. Cadogan and P.G. Hibbert, Proc. Chem. Soc., 1964, 338.

81 G. Wittig and R. Ludwig, Angew. Chem., 1956, 68, 40.

82 J.I.G. Cadogan, M.P.J. Harger and J.T. Sharp, Unpublished Observations.

83 J.A. Kampmeier and A.B. Rubin, Tetrahedron Letters, 1966, 2853; D.L. Brydon and J.I.G. Cadogan, Chem. Comm., 1966, 744.

84 R. Stoermer and B. Kahlet, Ber., 1902, 35, 1633; W.E. Bachmann and H.T. Clarke, J. Amer. Chem. Soc., 1927, 49, 2089; A. Lüttringhaus and G.V. Saäf, Annalen, 1939, 542, 250; A.A. Morton, J.B. Davidson, and B.L. Hakan, J. Amer. Chem. Soc., 1942, 64, 2242.

85 G. Wittig, Naturwiss., 1942, 30, 696.

86 G. Wittig, G. Pieper, and G. Fuhrmann, Ber., 1940, 73, 1193; G. Wittig and W. Merkle, Ber,, 1942, 75, 1491.

87 G. Wittig and G. Witt, Ber., 1940, 73, 1480.

88 H. Gilman and R.D. Gorsich, J. Amer. Chem. Soc., 1955, 77, 3919; 1956, 78, 2217.

89 F.W. Bergstrom, R.E. Wright, C. Chandler, and W.A. Gilkey, J. Org. Chem., 1936, 1, 170; R.S. Urmer and F.W. Bergstrom, J. Amer. Chem. Soc., 1945, 67, 2110; H. Gilman and J.F. Nobis, J. Amer. Chem. Soc., 1945, 67, 1479, 2106; H. Gilman, R.H. Kyle and R.A. Benkeser, J. Amer. Chem. Soc., 1946, 68, 143; H. Gilman and S. Avakian, J. Amer. Chem. Soc., 1945, 67, 349.

90 R.A. Benkeser and W.A. Buting, J. Amer. Chem. Soc., 1952, 74, 3011.

91 J.D. Roberts, D.A. Semenov, H.E. Simmons and L.A. Carlsmith, J. Amer. Chem. Soc., 1956, 78, 601; J.D. Roberts, H.E. Simmons, L.A. Carlsmith, and C.W. Vaughan, J. Amer. Chem. Soc., 1953, 75, 3290; J.D. Roberts, C.W. Vaughan, L.A. Carlsmith and D.A. Semenov, J. Amer. Chem. Soc., 1956, 78, 611.

92 M. Panar and J.D. Roberts, J. Amer. Chem. Soc., 1960, 82, 3629; R.A. Benkeser and G.S. Schrole, J. Amer. Chem. Soc., 1953, 75, 3196.

93 J.F. Bunnett and T.K. Brotherton, J. Org. Chem., 1958, 23, 904.

94 (a) G. Wittig and L. Pohmer, Angew. Chem., 1955, 67, 348; Ber., 1956, 89, 1334; (b) G. Wittig, Rer., 1958, 91, 883; (c) G. Wittig and E. Benz, Tetrahedron, 1960, 10, 37; Ber., 1959, 92, 1999; (d) E. Wolthuis, J. Org. Chem., 1961, 26, 2215; 1963, 28, 148; (e) H. Gilman and R.D. Gorsich, J. Amer. Chem. Soc., 1957, 79, 2625.

95 G. Wittig and L. Knaus, Ber., 1958, 91, 895.

96 V. Franzen and H.I. Joschek, Angew. Chem., 1960, 72, 564.

97 E. Wolthuis, D.V. Jagt, S. Mels, and A. de Boer, J. Org. Chem., 1965, 30, 190.

98 R. Huisgen and H. Rist, Annalen, 1955, 594, 137; R. Huisgen, J. Sauer, W. Mack, and I. Zeigler, Ber., 1959, 92, 441.

99 R.M. Stiles and R.G. Miller, J. Amer. Chem. Soc., 1960, 82, 3802; R.S. Berry, N. Spokes, and R.M. Stiles, J. Amer. Chem. Soc., 1960, 82, 5240; S. Yaroslavsky, Chem. and Ind., 1965, 765.

100 L. Friedmann and F.H. Logullo, J. Amer. Chem. Soc., 1963, 85, 1549.

101 E. le Goff, J. Amer. Chem. Soc., 1962, 84, 3786.

102 F.M. Beringer and S.J. Huang, J. Org. Chem., 1964, 29, 445.

103 G. Wittig and R.W. Hoffmann, Angew. Chem., 1961, 73, 435.

104 C.D. Campbell and C.W. Rees, Proc. Chem. Soc., 1964, 296.

105 C.D. Campbell and C.W. Rees, Chem. Comm., 1965, 193.

106 R.W. Hoffmann, Ber., 1964, 97, 2763; 1965, 98, 222.

107 G. Wittig and H.F. Ebel, Angew. Chem., 1960, 72, 564; Annalen, 1961, 650, 20.

108 J.A. Kampmeier and E. Hoffmeister, J. Amer. Chem. Soc., 1962, 84, 3787; G. Wittig and L. Pohmer, Angew. Chem., 1957, 69, 245.

109 G. Wittig and R. Ludwig, "Organic Syntheses"., John Wiley and Sons, Inc., New York, 1959, Vol.39, p.75.

110 M.G. Romanelli and E.I. Becker, J. Org. Chem., 1962, 27, 662.

111 G. Wittig and F. Behnisch, Ber., 1958, 91, 2358; G. Wittig and B. Reichel, Ber., 1963, 96, 2851; G. Wittig, E. Knauss, and K. Niethammer, Annalen, 1960, 630, 10, 951.

112 (a) R.M. Stiles, U. Burckhardt, and A. Haag, J. Org. Chem., 1962, 27, 4715; (b) G. Wittig and W. Merkle, Ber., 1943, 76, 109.

113 R.G. Miller and R.M. Stiles, J. Amer. Chem. Soc., 1963, 85, 1798; 1966, 88, 21; S. Meyerson and E.K. Fields, Chem. and Ind., 1966, 1230.

114 L. Friedmann, J. Amer. Chem. Soc., 1967, 89, 3071.

115 R. Huisgen and R. Knorr, Tetrahedron Letters, 1965, 1017.

116 H. Heaney and J.M. Jablonski, Tetrahedron Letters, 1966, 4529; J.P.N. Brewer and H. Heaney, Tetrahedron Letters, 1965, 4709; N.N. Vorozlitzov, V.A. Barklasch, N.G. Ivanova and A.K. Petrov, Tetrahedron Letters, 1964, 3575.

117 M. Stiles, R.G. Miller, and U. Burckhardt, J. Amer. Chem. Soc., 1963, 85, 1792.

118 V. Franzen, H.I. Joschek, C. Mertz, Angew. Chem., 1962, 74, 763.

119 W.W. Leake and R. Levine, J. Amer. Chem. Soc., 1959, 81, 1169.

120 E.A. Arnett, J. Org. Chem., 1960, 25, 324.

121 B.F. Hrutford and J.F. Bunnett, J. Amer. Chem. Soc., 1958, 80, 2021; R. Huisgen and H. König, Angew. Chem., 1957, 69, 268; J.F. Bunnett and B.F. Hrutford, J. Amer. Chem. Soc., 1961, 83, 1691.

122 I.T. Millar and H. Heaney, Quart. Rev. 1957, 11, 109.

123 G.A. Russell and R.F. Bridges, Tetrahedron Letters, 1963, 739.

124 R. Huisgen and J. Sauer, Angew. Chem., 1960, 72, 91.

125 G.B.R. de Graaf, H.J. Hertog and W. Ch. Melger, Tetrahedron Letters, 1967, 1477.

126 R. Adams and L.H. Ulich, J. Amer. Chem. Soc., 1920, 42, 606.

127 H. Meyer, Monatsh., 1901, 22, 779.

128 G.T. Morgan and E.A. Coulson, J. Chem. Soc., 1929, 2208.

129 J.S. Melt and W.B. Trapp, J. Amer. Chem. Soc., 1952, 74, 2686.

130 L.A. Tetyneva and P.A. Petyunin, Zhur. Obsh. Khim., 1958, 28, 739.

131 L.C. Raiford, R. Taft, and H.P. Lankelmg, J. Amer. Chem. Soc., 1924, 46, 2054.

132 Verkade, Wepster, and Witjens, Rec. Trav. Chim., 1951, 70, 139.

133 Angelo Mangini, Gazz. Chim. Ital., 1930, 66, 337.

134 Kichitaro Takatori, J. Pharm. Soc. Japan, 1954, 73, 810.

135 L.A. Tetyueva and P.A. Petyunin, Zhur. Obshchei. Khim, 1958, 28, 739.

136 J.R. Morton and H.W. Wilcox, "Inorganic Syntheses", McGraw-Hill Publishing Co. Ltd., London, 1953, Vol. 4, p.48.

137 W.S.M. Grieve and D.H. Hey, J. Chem. Soc., 1935, 691.

138 M. Kohn and I. Karlin, Monatsh., 1927, 48, 606.

139 M. Kohn and G. Dömöter, Monatsh., 1926, 47, 235.

140 L.C. Raiford and L. Rosen, J. Amer. Chem. Soc., 1946, 68, 397.

141 W.H. Hunter and F.E. Joyce, J. Amer. Chem. Soc., 1917, 39, 2642.

142 M. Mousseron and R. Jacquer, Bull. Soc. Chim. France, 1951, 106.

143 V.P. Malik and G.S. Saharia, J. Sci. Ind. Research (India), 1956, 15B., 633.

144 N. Neeman and A. Modiano, J. Org. Chem., 1956, 21, 667.

145 Taizo Matsukaiva, Shoichi Ban, and Toshiro Imada, J. Pharm. Soc. Japan, 1951, 71, 477.

146 H. Hodgson and A.P. Mahadevan, J. Chem. Soc., 1947, 174.

147 W.F. Huber, M. Renoll, A.G. Rossow, and D.T. Moury, J. Amer. Chem. Soc., 1946, 68, 1111.

148 "Chemistry of Carbon Compounds", Elsevier Publishing Co., London, 1951, Vol.1, p.98.

149 S.J. Holt and P.W. Sadler, Proc. Roy. Soc. (London), 1958, 148, 481.

150 "Dictionary of Organic Compounds", Eyre and Spottiswoode, Ltd., E. and F.N. Spon Ltd., London, 1965

151 S. Chang, D.H. Hey, and G.H. Williams, J. Chem. Soc., 1958, 1385, 2600, 4403.

152 A. Hantzsh and J.S. Smythe, Ber., 1900, 33, 505.

153 D.L. Brydon, Ph.D. Thesis, St. Andrews, 1967.

154 J.A. Zoltewicz and J.F. Bunnett, J. Amer. Chem. Soc, 1965, 87, 2640.

155 A. Vogel, "Practical Organic Chemistry", Longmans, Green and Co. Ltd., London, 1956, p. 582, 780.

156 A. Vogel, "Practical Organic Chemistry", Longmans, Green and Co. Ltd., London, 1956, p.1064.

157 J.I.G. Cadogan, D.A. Roy and D.M. Smith, private communication.

158 E. Bamberger, Ber., 1895, 28, 1222.

159 M. Aroney, R.J.W. Le Fèvre, and R.L. Werner, J. Chem. Soc., 1955, 276; K.B. Whetsel, G.F. Hawkins, and F.E. Johnson, J. Amer. Chem. Soc., 1956, 78, 3360.

160 H. Suschitzky, Angew.Chem. Internat. Edn., 1967, 3, 581.

161 R.W. Franck and K. Yanagi, Tetrahedron Letters, 1966, 2905.

162 H. Zollinger, "Diazo and Azo Chemistry", Interscience Publishers, Ltd., London, 1961, p.141.

163 G.H. Williams, "Homolytic Aromatic Substitution", Pergamon Press, London, 1960.

164 Houben-Weyl, "Methoden der Organischen Chemie", Georg Thieme, Stuttgart, 1965, Vol. 10/3, p.99.

165 E. Wolthuis, J. Org. Chem., 1961, 26, 2215.